CHARACTERIZATION OF AN ELECTROSPRAY WITH CO-FLOWING GAS

by

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Mechanical and Industrial Engineering
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Abstract

In mass spectrometry an electrospray is commonly used as an ion source. At high sample flow rates a sheath co-flow of gas around the electrospray emitter is employed. The co-flow of gas reduces contamination and increases signal sensitivity in the mass spectrometer’s results. This work characterizes the operation of an electrospray with co-flowing air for various operating conditions. It is found that a co-flowing air has a negligible effect on droplet size for the spindle and cone jet modes while it only reduces the droplet size marginally in the unstable mode. In the high flow rate unstable mode, the addition of air seems to have no real effect on droplet size. In summary, the electrospray with co-flowing air produces a denser and more focused spray with similar droplet size and distribution than that of the un-nebulized spray. This explains why using co-flowing air in mass spectrometry applications improves the signal quality, since it allows for the focusing of droplets produced into the inlet and also aids in the breakup of larger droplets.
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1 Introduction

1.1 Electrostatic Sprays

An electric field can be used to atomize a fluid that issues from a capillary, creating a wide range of sprays. Such sprays are known as Electrosprays (ES). Depending on the fluid properties, electric field and the surrounding medium, various modes of spraying can be achieved. Descriptions and classifications of these spraying modes can be found in the literature [1, 2, 3, 4, 5, 6, 7, 8, 9, 10] [11] with initial investigations on the subject dating back to 1878 with the study of the breakup of electrified liquid jets [12]. The practical applications of electrosprays has grown continually over the past century and includes spray painting, fine powder production, micro and nano film deposition, mass spectrometry, thrusters for small spacecraft, air purification and agricultural sprays. One of the key features of an electrospray, compared with other spray technologies, is that it has the ability to produce extremely small droplets, even from a relatively large capillary, and also to produce mono-dispersed sprays.

In mass spectrometry applications, electrosprays are used to introduce sample and solvent mixtures (solutions) into a mass spectrometer’s inlet. In order for the mass spectrometer to efficiently analyze the sample, the size of the droplets becomes very important. In general, the smaller the droplet sizes the better, because this will cause the solvent to evaporate from the drops at a higher rate. Once the solvent is evaporated, all that remains is the ionic form of the sample, which is then drawn into the mass spectrometer inlet via a pressure difference. If the droplets are too large, then the solvent may not have enough time to evaporate sufficiently before the drop is drawn into the mass spectrometer. If this is the case, then the ions within the droplets may not get released, which negatively affects the mass spectrometer’s performance. The higher the liquid flow rate, the more difficult it becomes to operate the electrospray in a mode that produces the desired mono-dispersed, small charged droplets [13]. Instead, at higher liquid flowrates, the electrospray operates in an undesirable unstable mode. The droplets produced in the unstable mode have the desired charge on the sample, but the droplets also tend to be larger. In practice, the liquid flow rates used in mass spectrometry are relatively high and, therefore, the electrospray usually operates in the unstable mode. Another issue when using an electrospray is that the charged droplets may not enter into the inlet of the mass spectrometer. Since the droplets are
charged, they get attracted towards any surface with a lower charge potential and, therefore, may travel away from the inlet.

To resolve some of the mentioned issues, a co-flow of gas around the electrospray nozzle is frequently used. This co-flow of gas assists in fluid breakup, enhances solvent evaporation from the droplets and also directs the spray droplets towards the inlet of the mass spectrometer. Ikonomou et al studied the effects of using a nebulized electrospray on the final signal sensitivity output by the mass spectrometer [13]. However, there was no analysis of the effect of co-flowing air on characteristics of the electrospray structure in terms of droplet size and velocity. Tang et al studied the effects of a sheath co-flow of gas around the electrospray nozzle [14, 15]. They used the sheath co-flow of gas as a way to modify the local electrical breakdown voltage around the electrospray. In doing so, they were able to modify the electrospray operating mode such that it would operate in the desired cone jet mode. They compared electrospray characteristics between an un-nebulized and nebulized electrospray operating in the cone jet mode. The electrospray system studied in this thesis used the same emitter design as that used in mass spectrometry applications where the electrospray is mainly operated in the high flow rate unstable mode. The effect of co-flowing air on the structure and characteristics of various electrospray operating modes, including the high flow rate instable mode, is the focus of this work.
1.2 Electrospray Mechanism

When an ionic solution is exposed to an electric field, the positive and negative ions will experience Coulombic forces, which will cause them to move in the solution [16]. This is known as the electrophoresis effect [17]. The strength of these forces will depend on the applied electric field strength and also the charge in the individual ions. The following figure shows a hypothetical fluid droplet, containing ions, in an electric field created by two oppositely charged plates:

Figure 1-1: Electrophoresis of a droplet in an electric field. The positive and negative ions move towards the negative plate and positive plate respectively.

In Figure 1-1, the positive and negative ions will experience a Coulombic electrostatic force \( F_E \) given by:

\[
F_E = q\overrightarrow{E}
\]

(1-1)

In Figure 1-1, the positive ions will experience a force in the direction of the electric field flux, therefore towards the negatively charged plate and the negative ions experience a force in the opposite direction. If they were free to travel without any restrictions, as in a vacuum, these ions would move all the way to the charged plates to reduce their electrostatic potential energy to zero. In this case however, the droplet is considered to be in air that is at room temperature and pressure, and there are many forces impeding the ion movements within and outside the droplet. Within the droplet, the ions experience forces due to friction and partial pressure forces between the molecules, as well as electrostatic forces between the other ions in the fluid [16]. Even after
overcoming these impeding forces, if an ion makes it to the liquid/air interface at the drop surface, the liquid surface tension $\gamma$ has to be overcome. Further information on the various electrostatic and non-electrostatic forces affecting droplets can be found in the referred book [18].

### 1.2.1 Spray Formation

When the ions are at the fluid/air interface they form an electric double layer [18], where they apply an electrostatic force on the interface that opposes the surface tension forces and deforms the drop. If a large enough electric field is applied, these ions can actually overcome the surface tension forces altogether and break through the liquid/air interface barrier [19]. This is essentially what happens in an Electrospray (ES), also called Electrohydrodynamic Spray (EHD), and the phenomenon is illustrated in Figure 5-1.

![Electrospray mechanism](image)

**Figure 1-2: Electrospray mechanism [20]**

In Figure 1-2, the capillary at the top of the figure contains an ionic liquid whose ions are under the influence of an electric field created by the high voltage power supply. This field is created between the capillary and the ground plate. The positively charged ions at the capillary migrate to the liquid/air interface and deform the fluid surface into a conical shape.
Sir Geoffrey Taylor extensively studied and characterized the conical shape an electrified fluid interface takes [21] and in his honor, this conical shape is referred to as a Taylor cone. Taylor stated, and proved experimentally, that the cone shape is the equilibrium shape that the meniscus fluid/air interface assumes when a strong enough electric field is applied to it. Taylor also determined the theoretical half-cone angle for equilibrium, which is 49.3°. When a Taylor cone begins to form, the electric field strength is such that the electrostatic force at the fluid/air interface, due to the ions, is exactly balanced by the surface tension force [11]. This electric field strength $E_{on}$ is called the field strength for the onset of electrospray and it is dependent on the surface tension of the ionic solution used, as expected, as well as the capillary radius. The electric field strength $E_0$ can be approximated by the following relationship [11]:

$$E_{on} = \left( \frac{2\gamma \cos \theta}{\varepsilon_0 r_c} \right)^{\frac{1}{2}} \quad (1-2)$$

Following from the electric field strength required for the onset of an electrospray, the voltage $V_{on}$ required for the onset of an electrospray can be approximated as follows, where $d$ is the distance of the ground electrode from the capillary tip [11]:

$$V_{on} = \left( \frac{r_c \gamma \cos \theta}{2\varepsilon_0} \right)^{\frac{1}{2}} \ln \left( \frac{4d}{r_c} \right) \quad (1-3)$$

After the Taylor cone is formed, a slightly further increase in the electric field can cause the ions to break through the liquid/air barrier and move freely under the influence of the electric field in the air. At the capillary and ground plate surfaces, the ions complete reduction and oxidation reactions and, therefore, resemble an electrolytic cell. The nature of these reactions is described in detail in the referred work [20].

Notice in Figure 1-2 that the initial ejections from the Taylor cone show drops that contain multiple ions of the same charge and not just single ions, as expected. This is due to the high free energy required to bring an ion from the liquid phase into the gas phase [17]. It takes far less energy to free clusters of solvated ions. From now on solvated ions will be referred to simply as charged drops.
1.2.2 Spray Current, Droplet Radius and Droplet Charge

As expected from the above discussion, the occurrence of ES has been shown to depend on the presence of electrolytes, and therefore ions, in the fluid with a minimum concentration of $10^{-5}$ mol l$^{-1}$ [13]. When the mentioned minimum concentration is met, on the basis of theoretical reasoning and experimental measurements [22], the following relationship for spray current $I$, drop radius $R$ and droplet charge $q$ has been proposed:

\[ I \approx f \left( \frac{\varepsilon}{\varepsilon_0} \right) \left( \gamma \sigma Q \frac{\varepsilon}{\varepsilon_0} \right)^{\frac{1}{2}} \]  
\[ R \approx \left( \frac{Q\varepsilon}{\sigma} \right)^{\frac{1}{3}} \]  
\[ q \approx 0.7 \left[ 8\pi(\varepsilon_0 \gamma R^3)^{\frac{1}{2}} \right] \]

Where $f \left( \frac{\varepsilon}{\varepsilon_0} \right)$ is a numerical function which has been tabulated [22]. For liquids whose dielectric constant is $\frac{\varepsilon}{\varepsilon_0} \geq 40$, $f \left( \frac{\varepsilon}{\varepsilon_0} \right) \approx 18$. These relationships are valid when the electrospray is operated in the cone jet mode [22]

1.2.3 Forces at the ES Capillary Tip

At the ES capillary tip, the fluid meniscus is exposed to a variety of different forces. First, if we consider no electric field applied at the capillary tip, then we have the effect of hydrostatic pressure and surface tension. The hydrostatic pressure will cause the meniscus to grow as more fluid flows into the emerging drop. The surface tension keeps the drop connected to the main fluid body in the capillary until a certain critical limit, when the gravitational force of the drop overcomes the surface tension and the top of the drop necks and separates from the capillary tip. This phenomenon has been studied in great detail in the referred work [23]. If an electric field is now applied to the capillary tip, an added electrostatic force now comes into play. The electrostatic force, as described previously, acts against the surface tension forces to deform the meniscus liquid/air interface. The deformation of the meniscus, under a constant electric field, depends on
various liquid properties such as the viscosity, conductivity, dielectric permeability and surface tension.

1.2.4 Electric Field at the ES Capillary Tip

The electric field at the capillary tip depends on the geometry of the capillary, the distance of the ground electrode from the capillary tip, the geometry of the ground electrode and also the applied voltages. To calculate the electric fields at the capillary tip, mathematical models and analytical solutions have been developed [11][24]. In the case of certain geometrical setups, it is possible to approximate the electric field $E_c$ at the capillary tip. One such case is when the ground electrode is very large and planar in relationship to the capillary tip. In this case, the electric field can be approximated using the following relationship:

$$ E_c = \frac{2V_c}{r_c \ln \left( \frac{4d}{r_c} \right)} \quad (1-7) $$

This relationship is valid when the ground electrode is sufficiently large enough to be considered planar [25].
2 Electrospray Spraying Modes

2.1 Spraying Modes

Depending on the fluid properties and other experimental conditions in an electrospray system, many different electrospray spraying modes have been observed [26, 7]. A brief overview of the various spraying modes will be presented, but for more details on the specific types of spraying modes see the referred work. The various spraying modes for an electrospray are a function of the following:

- Fluid properties (both spray fluid and surrounding fluid)
  - Electrical conductivity
  - Surface tension
  - Viscosity
  - Dielectric constant
- Other parameters
  - Electric field
    - Field strength applied at the capillary tip
    - Field properties in the area of the electrospray
  - Capillary geometry
  - Fluid flow rate
  - Co-flowing air

By varying all of the mentioned parameters, one can obtain a dynamic range of spraying modes. If you vary only the electric field strength at the capillary tip and fix all the fluid properties and other parameters, the modes of electrospray operation you can expect are summarized in Figure 2-1.
Figure 2-1: The various electrospray modes that can be observed by varying the electric field strength applied at the capillary orifice

The following is a brief description of all the major spraying modes identified in the literature in order of increased electric field applied to the capillary tip.

2.1.1 Dripping Mode

A relatively low strength electric field applied at the capillary tip will cause the pendant drops to pinch off at a faster rate than without an electric field. This is due to the added electrostatic force of the ions in the drop, as previously explained. By increasing the electric field strength, the drop frequency increases and the radius decreases.

2.1.2 Spindle Mode

This mode is also known as the pulsating mode. In this mode, the shape of the meniscus is constantly pulsating between a hemispherical shape and a cone shape [21]. The reason for the pulsation is due to the imbalance in forces between the surface tension and electric charge of the ions. Once the cone shape is achieved by the electrostatic force of the ions, a jet is emitted in which most of the ion close to the surface are ejected, and therefore the electrostatic force decreases and the surface tension force pulls the meniscus inwards back to a hemispherical shape. New ions then migrate to the meniscus, deforming its shape back to a cone shape and the whole process repeats itself.
2.1.3 Cone-Jet Mode

2.1.3.1 General

This mode of electrospray operation is one of the most interesting and well studied of all. It is when the meniscus at the liquid/air interface takes the form of a Taylor cone and emits a steady jet of liquid from its apex. This jet of liquid travels a certain distance below the cone apex before breaking up into droplets.

2.1.3.2 Breakup of jets into droplets

If the charge of the jet is not too high, the breakup of the initial drops takes place by the same Rayleigh jet instability mechanism as for a neutral jet. The droplet diameter can be related to the jet diameter in this case by the following relationship:

\[
\frac{\phi_D}{\phi_J} = \left(\frac{3k\sqrt{3}}{2}\right)^{\frac{1}{3}}
\]

In equation (2-1) the relationship of the droplets produced to the jet diameter in the cone-jet spraying mode [10]. For low viscosity (inviscid) liquids, the value of k is estimated to be 4.5 [10], which leads to the following ratio:

\[
\frac{\phi_D}{\phi_J} = 1.89
\]

Equation (2-2) shows the relationship for the ratio of droplets produced to jet diameter in a varicose instability type cone-jet. This relationship has been shown to correlate very closely with values measured through experiment [10].

2.1.3.3 Droplet charge

By assuming that all the droplets have the same size and applying the minimization of energy principle, the following relationship between the charge-to-volume ratio of a drop has been established [27]:

\[
\frac{q}{v} = 6(2e_A\sigma \phi_D^{-3})^{\frac{1}{2}}
\]
Equation (2-3) shows the relationship between a droplet’s charge-to-volume ratio and its diameter [27]. As shown by experiments done, [2][28] the above relationship is not fully justified, as the droplet charging is greatly dependent on production conditions and can vary from one drop of a certain size to the next.

The above relationship, however, can be used in another way as follows. The current measured at the ground electrode is equal to the current carried by the charges in the drops; therefore the ratio of current-to-flow rate is equal to charge-to-volume. If these ratios are switched in the relationship shown in Equation (2-3), then you end up with the following:

\[
\phi_D = \left[6(2\varepsilon\sigma)^{\frac{1}{2}}Q^{\frac{2}{3}}I\right]^{\frac{1}{2}}
\]  

(2-4)

Equation (2-4) shows the relationship of the diameter of a drop to current and flow rate of the electrospray system [10]. Q is the liquid flow rate and I is the measured current in the electrospray system. The above relationship gives the average emitted droplet size to the correct order of magnitude.

2.1.3.4 Effects of corona discharge

If a corona discharge occurs at the outlet of the capillary, the electric field is reduced significantly as the surrounding medium is ionized. If this happens, the following two phenomenons can occur [10]:

a) If the corona discharge occurs before the cone-jet mode is established, then the cone-jet mode may be prevented from being established at all.

b) If the corona discharge occurs after the cone-jet mode is established, then there may be fluctuations in the discharge current. The cone-jet mode can be stabilized by increasing the electric field strength in this case.

2.1.3.5 Multi-jet or multi-cone-jet

After the establishment of the cone-jet electrospray mode, if the electric field is further increased in strength, several more jets may begin to be emitted from the capillary tip simultaneously. In this case, the Taylor cone shrinks and splits up between the various emitted jets.
2.1.3.6 Droplet Size and Distribution in Cone-Jet Mode

One of the reasons that an electrospray is such a useful tool is the relatively small and evenly distributed droplets it is able to produce. Using a Phase Doppler Anemometer (PDA) system, Keqi Tang has been able to characterize the droplets of electrospray produced from Heptane and Methanol [15]. The results of these experiments show that the spray droplets are highly monodispersed as they travel from the emitter tip to the ground electrode.

2.1.3.7 Stability of the cone-jet mode

The cone-jet mode is achieved only when the operational and fluid parameters are within certain ranges. For fixed geometric and fluid properties and also for a fixed flow rate, varying the electric field strength applied at the emitter tip will determine which mode of operation the electrospray is in. For a particular electric field strength range, a stable cone-jet mode of operation will be achieved. Below this range you will fall into the spindle and dripping modes of operation. Above this range you will go into the unstable modes of operation. If you change the flow rate of the electrospray system, while keeping other parameters constant, the stable electric field strength range will change. By varying the flow rates and electric field strength you can determine all the field ranges at all possible flow rates for which a stable electrospray can be achieved. This stable electric field strength range for all available flow rates, where the cone-jet mode is observed, is known as the electrospray stability island. The main factors affecting the stability island of an electrospray system is the fluid properties themselves and, in particular, the surface tension and conductivity. The fluid surface tension directly affects the ability of a fluid to atomize in an electrospray because it opposes the force applied by the ions at the fluid/air interface. Therefore, increasing the surface tension will increase the required field strength for a cone-jet mode to be established. The conductivity of the fluid used has the effect of shifting the electrospray stability island to a narrower range and also to lower flow rates.

2.1.3.8 Effect of Viscosity

Increasing the viscosity of the fluid used in an electrospray has the effect of dramatically increasing the droplet sizes produced and therefore the ligament breakup. A dimensionless number has been proposed [29] to determine the importance of viscosity on the electrospray ligament breakup:
\[ \pi_\mu = \left( \gamma^2 \rho \frac{\varepsilon \varepsilon_0}{\sigma} \right)^{\frac{1}{3}} \mu \] (2.5)

When \( \pi_\mu \) is much greater than 1 then viscous effects are negligible.

2.1.3.9 Effect of Conductivity

As mentioned previously, the effect of increasing the conductivity of the electrospray fluid decreases the flow rate and also narrows the electric field strength range at which a stable cone-jet mode can be established. Another effect of increasing conductivity is that the filament jet radius emitted from the cone tip decreases and this in turn decreases the droplet size produced [15].

2.1.3.10 Effect of Surface Tension

As previously mentioned, the effect of increasing the electrospray fluid surface tension tends to increase the electric field strength required to create a stable cone-jet mode. If a fluid has a sufficiently large surface tension, such as distilled water (\( \approx 0.074 \text{ Nm}^{-1} \) at \( 20^\circ \text{C} \)), the ionization potential of the air around the electrospray is reached before any kind of electrospray is created and, therefore, a stable cone-jet mode is difficult and almost impossible to create without the use of some sheath co-flowing gas around the electrospray system.

2.1.3.11 Effect of Flow Rate

Increasing the flow rate of the fluid increases the diameter of the jet emitted from the Taylor cone and, therefore, the droplets produced by the electrospray [15].

2.1.4 Unstable Modes

2.1.4.1 Kink Instabilities

This type of mechanism is present when the electrostatic pressure in the jet approaches the capillary pressure. In this mode of electrospray operation, after the largest droplets have just separated from the jet, their charge is such that they exceed the Rayleigh limit [12]. They then emit a jet themselves that resembles a miniature Taylor cone, which breaks up into even finer drops. If the
electrical field strength is slightly higher, lateral kink-type instabilities appear. These instabilities constitute a whipping jet that winds and thins out, eventually disintegrating onto finer droplets.

2.1.4.2 Simple Jet and Ramified Jet

When no electric field is applied at the capillary, the liquid may be emitted in the form of a jet if a high enough fluid flow rate is achieved. This is the critical flow rate at which the kinetic energy of the fluid is greater than the surface energy to create the jet surface [30]. When this jet is formed, an electric field applied to it will charge and accelerate it.
3 From Charged Droplets to Gas Phase Ions

3.1 Solvent Evaporation

The charged droplets produced by an electrospray shrink, due to solvent evaporation, while the droplet charge remains constant. The energy required for the solvent evaporation is provided by the thermal energy of the ambient air. The charge on the droplets is assumed to remain constant because the emissions of ions from solution to the gas phase is highly endothermic [31]. From kinetic theory, for droplet evaporation, the time required for an initial droplet with radius $R_0$ to reach size $R_1$ can be estimated by the following equations [32]:

$$\frac{dR}{dt} = \frac{-\alpha v P^0 M}{4\rho R_g T} \quad (3-1)$$

$$R_1 = R_0 - \frac{\sigma v P^0 M}{4\rho R_g T} \quad (3-2)$$

The relationships (3-1) and (3-2) are for the radius of a drop undergoing solvent evaporation. Where $v$ is the thermal velocity of solvent vapor, $P_0$ is the saturation vapor pressure of the solvent at room temperature, $M$ is the molar mass of the solvent, $\rho$ is the density of the solvent, $R_g$ is the gas constant, $T$ is the temperature of the drop and $\alpha$ is the condensation coefficient of the solvent ($\alpha \approx 0.04$ for water, ethanol and probably methanol [33]). The rate of droplet evaporation has been shown to depend greatly on the initial droplet diameter [15]:

$$\frac{dd}{dt} = -\frac{K}{d} \quad (3-3)$$

Equation (3-3) shows the droplet rate of evaporation relationship where $K$ is the constant of evaporation [15]. In this relationship, the rate of droplet evaporation is inversely proportional to the droplet diameter.
3.2 Droplet Instability and the Rayleigh Limit

The decrease of the droplet radius $R$ at constant charge $q$ leads to an increase of the electrostatic repulsion of the charges at the droplet surface until the droplet reaches the Rayleigh stability limit [34] given by:

$$q_r = 8\pi(\varepsilon_o\sigma R^3)^{\frac{1}{2}}$$  \hspace{1cm} (3-4)

At this critical radius, the charged droplet becomes unstable. It has been experimentally observed that the droplets undergo an uneven fission [33] when they are close to the Rayleigh limit.

3.3 Aerodynamic Effect on Droplets

Since this thesis deals with the effect of co-flowing air on the electrospray operating modes, the aerodynamic effects of a gas on fluid drops are briefly discussed here. The aerodynamic deformation effect on a moving droplet can be defined by the Weber’s number:

$$W_e = \frac{\rho g D U_r^2}{\sigma}$$  \hspace{1cm} (3-5)

When the Weber number is greater than a critical value, which is in the order of ten [35], the aerodynamic force will overcome the surface tension force and deform the droplet. In order to evaluate the aerodynamic effect on a charged droplet, we need to introduce an effective surface tension $\gamma_e$ which takes into account the electrostatic force on the drop surface due to charge [15]. The electric pressure acting on the droplet surface due to the surface charge is:

$$P_e = \frac{1}{2}\varepsilon_0 E^2 = \frac{1}{2}\varepsilon_0 \left(\frac{q}{\pi\varepsilon_0 D^2}\right)^2$$  \hspace{1cm} (3-6)

The electric pressure force acts in the direction opposite to the surface tension force and therefore has the effect of reducing the surface tension. Taking this into account, an effective surface tension $\sigma_e$ can be introduced as follows:

$$\sigma_e = \sigma_0 - \frac{q^2}{8\pi^2\varepsilon_0 D^2}$$  \hspace{1cm} (3-7)
In Equation (3-7), $\sigma_o$ is the surface tension of the fluid and $\sigma_e$ is the effective surface tension due to the electric pressure acting against the fluid surface tension. The effective surface tension is affected by two main properties of the drop; charge and diameter. As the diameter of the drop decreases, it has been shown previously that the droplet reaches the Rayleigh limit and then undergoes a Coulombic explosion. This Coulombic explosion indicates that the surface tension of the droplet has been overcome by the surface charge pressure and hence the effective surface tension is zero at the Rayleigh limit. If we substitute the Rayleigh limit equation in (3-4) into the effective surface tension equation (3-7) we get:

$$\sigma_e = \sigma_o \left(1 - \frac{q^2}{q_r^2}\right)$$

(3-8)

The relationship obtained in equation (3-8) shows that the effective surface tension for a droplet is dependent on how close the droplet charge is to the Rayleigh limit charge. If the Weber number equation is rearranged and the critical Weber number, at which aerodynamic forces become important, is treated as a constant we get the following:

$$\sigma_{cr} = \frac{\rho g D U_r^2}{W_{r,cr}}$$

(3-9)

To estimate the aerodynamic effect on a charged droplet, the effective surface tension can be calculated using the relationship in equation (3-8) and compared with the critical surface tension in (3-9). If the effective surface tension is much lower than the critical surface tension, $\sigma_e \leq \sigma_{cr}$, then the aerodynamic effects on the drop are important and conversely if, $\sigma_e \geq \sigma_{cr}$, then the aerodynamic forces are negligible.

### 3.4 Mechanisms for the Formation of Ions

After the droplets have undergone a few jet fissions, they are so small that they have not been directly observed by experimental observation, as mentioned before. This has led to the creation of two main theories to what happens next to these highly charge small droplets.

The first theory is the charged residue model (CRM) first proposed by Dole [36], who was one of the first people to study the gas phase ion production in ES. In Dole’s model, the droplets under-
go jet fission until very small droplets on the order of a few nano meters are created. These drops now contain only single ions. Continuing solvent evaporation from these drops yields a single gas phase ion.

The second theory is based on the ion evaporation model (IEM) proposed by Iribarne and Thompson [37]. In IEM after the radius of the charged droplets has reduced to the order of tens of nano meters, due to solvent evaporation and jet fission, direct ion emission to the gas phase from the droplets becomes possible. The theory says that IEM becomes dominant over jet fission for droplets of radii $R \leq 10$ nm [33]. The following figure illustrates the two different theories of gas phase ion evolution in an ES [38]:

![Diagram illustrating the CRM and IEM theories of gas phase ion generation from charged electrospray droplets.](image)

Figure 3-1: The CRM and IEM theories of gas phase ion generation from charged electrospray droplets.

The overall predictions for obtaining gas phase ions from charged droplets due to the CRM theory and the IEM theory are only distinctly different for certain conditions. For charged droplets of radii $\geq 10$ nm, the CRM model is favorable and for radii $\leq 10$ nm, the IEM theory is favorable. For radii $\leq 1$ nm, there are so few ions compared with solvent molecules that neither the
IEM theory nor CRM theory strictly apply, however the process is closer to the IEM theory [33].

4 Electrosprays in Mass Spectrometry

4.1 Overview

A mass spectrometer requires molecules in the ionic form, so they can be detected and analyzed. The method of obtaining these ions has a large effect on the overall performance of the mass spectrometer. Before the use of ES as an ion source, mass spectrometers used methods such as fast atom bombardment (FAB) and plasma desorption [33] to obtain ions. These earlier methods for creating gas phase ions required high energy collisions and high localized heating which led to additional processes such as the creation of ions from neutral molecules of non-interest and fragmentation of ions of interest. An ES ion source on the other hand creates ions without imparting any extra internal energy to them and therefore avoids any fragmentation of the ions or unwanted ions created from neutral molecules.

Once the gas phase ions are created, they are analyzed through the use of various available methods such as through the use of a quadrupole, time of flight analysis, Fourier transform ion cyclotron resonance, and also a magnetic sector [33]. For a detailed description of how these various methods work, the reader is directed to the referred work, however a brief description of each method is presented to illustrate why having the molecules in ionic form is the key to mass spectrometry.

4.2 Magnetic Sector

A charged molecule or ion will experience an electromagnetic force as it passes through a magnetic field and hence move under the influence of this field and accelerate. The rate of acceleration for two identically charged ions depends on the mass of the ions, and the magnetic sector mass spectrometer takes advantage of this fact. In a magnetic sector mass spectrometer, the ion source produces the gas phase ions for analysis, which is where the electrospray would be located. The ion optics accelerates the ions with a certain accelerating voltage. The accelerated ions are then deflected by the magnetic fields created by the magnet. An ion will only arrive at the ion detector if it has the right speed as it passes through the magnetic sector and also only if it
is deflecting the right amount. The ions speeds are determined by their masses because all the ions are accelerated by the same driving voltage and the amount of deflection the ions experience will depend on their charge because the magnetic field is kept constant. Therefore, by scanning the accelerating voltage through a wide range, you will only allow certain ions of a specific mass to charge ratio (m/z) at each accelerating voltage level. The detected abundance of ions at each specific mass-to-charge ratio creates a mass spectrum of all the ions in the molecule being analyzed and hence an analysis of the molecule itself.

4.3 Quadrupole

A quadrupole mass spectrometer uses varying electric fields to filter and detect various ions of different mass to charge ratios. This method uses superimposed dc and ac voltages applied to the two pairs of parallel rods, which creates a specific time varying electric field through which ions must pass. By varying the electric field, only ions of a specific mass-to-charge ratio will be stable and all others will be thrown off course into the bars or to the sides of the machine. Using this method, the quadrupole selectively filters different mass-to-charge ratios and therefore creates a mass spectrum by this method.

4.4 Fourier Transform Ion Cyclotron resonance

In this type of mass spectrometer, the ions are induced into a cyclotron resonance using magnetic fields. The resonating ions then produce specific time domain signals, depending on their mass-to-charge ratios. All of these signals are coupled into one master time domain signal which can be detected and analyzed using a Fourier transform to separate the individual components relating to the different ions.

4.5 Advances in Electrospray Mass Spectrometry

Half of all chemical and biochemical processes involve ions in solution [33], and one of the most promising and important applications of the ES process is in the mass spectrometry of these ions [39]. John Fenn received the 2002 Nobel Prize in Chemistry for his pioneering works in using an ES coupled with a mass spectrometer to detect large bio-molecules. Thanks to John Fenn’s work and all the related work that subsequently followed, the ES is now a standard choice for the production of gas phase ions for the inlet to a mass spectrometer.
When an electrospray is used to spray molecules into charged droplets, the process does not damage the molecules themselves and therefore, a sample is preserved until detection. An electrospray also has the ability to multiply charge molecules that are very large. This is a great advantage, as all mass spectrometers have a limited mass-to-charge ratio detection range. Multiple charging allows for the detection of large molecules as the mass-to-charge ratio for a molecule with a large molecular mass will reduce as its charge increases [39].

4.5.1 Mass Spectrometer Performance

In order to produce the best mass spectrum analysis results, the mass spectrometer requires as many detectable gas phase ions as possible. To produce the gas phase ions, the electrospray should be operating in a way that produces mono-dispersed uniform droplets, and also droplets small enough that can evaporate and reach the Rayleigh stability limit quickly. In a mass spectrometer, the operating conditions for the electrospray is affected by a wide range of variables already mentioned, such as the fluid properties, flow rate, electric field and ambient temperature and pressure. These variables have a large effect on the droplet evaporation and hence the ion formation from the droplets. A variety of electrospray setups have been developed and used in modern mass spectrometers to maximize the gas phase ion production and therefore the quality of the mass spectrum analysis. Some of these methods will be presented in the following section.

4.5.2 Drying Gas

To aid with evaporation and maximize the gas phase ion production from the charged droplets, most mass spectrometers use some mechanism for supplying dry gas, usually nitrogen, to the spray area. With the use of a drying gas, the charged electrospray droplets evaporate faster and therefore, reach a smaller size more quickly, producing gas phase ions.

4.5.3 Temperature, Co-flowing Sheath Gas and Orthogonal Injection

Increasing the ambient temperature around the electrospray emitter in a mass spectrometer will also improve the production of gas phase ions by increasing the available energy for evaporation. Co-flowing sheath gas flow around the emitter orifice can be used in situations where a stable electrospray in the cone-jet mode is difficult to achieve. One reason why a stable cone-jet can be difficult to obtain is increased flow rates in mass spectrometer applications. An increase in flow
rate causes the electrospray to operate outside of the island of stability and, therefore, not in the desired cone jet mode. It has been shown that using a co-flowing sheath gas improves the production of gas phase ions [13]. In fact, even when there is no electric field applied (at zero capillary voltage) the co-flowing sheath gas electrospray still produces a signal at the mass spectrometer’s detector.

4.5.4 Orthogonal Injection

This design uses the momentum of the smaller gas phase ions as a way to separate them from the main flow of electrospray droplets. Traditionally, when an electrospray is aimed directly at the inlet to the mass spectrometer, there can be unwanted solute droplets, as well as ion containing solute droplets that never release their ions, sampled into the system and clouding the results and creating problems in cleaning the equipment. To avoid these issues most designs now use orthogonal injection, where the main electrospray flow is injected orthogonally to the mass spectrometer inlet and only the lighter gas phase ions produced are sucked in via the pressure difference, between the high pressure outside of the mass spectrometer inlet, and the lower pressure inside.
5 Apparatus and Procedures

5.1 Experimental Setup

The following describes our experimental setup and procedures. Fluid is supplied to the emitter orifice (150 µm I.D diameter and 300 µm O.D steel capillary tube, Sciex) at the desired constant flow rate via a syringe pump (Model 341B, Sage Instruments). The pump flow rate Q can be set from 1.8 std µl min$^{-1}$ up to 30000 std µl min$^{-1}$. A high power DC voltage supply (Series ER, Glassman High Voltage Inc.) is used to charge the emitter orifice at a desired voltage. The voltage can be varied from 0 to 10 kV. The ground electrode is positioned directly below the emitter orifice at a distance d that can be modified through the use of a Newport positioning stage. The grounding electrode is made of Aluminum and has a rectangular geometry (165 cm length x 109 cm breadth 1 cm thick). Co-flowing air is introduced around the emitter orifice through the use of a rotameter (Model FL-3845G-HRV, Omega), which is connected to a compressed air supply.

To view the electrospray, a high speed camera (Fastcam Ultima 1024, Photron Ltd) is used. The camera is connected to a long distance microscope (QM-100, Questar), which in turn is attached to a set of Newport positioning stages. The positioning stages give you accuracy to a micrometer in order to position the focal point of the camera directly on the emitter orifice. A light source is placed directly behind the emitter orifice, pointing towards the microscopic objective lens. With this setup it is possible to capture the dynamic structures of the electrospray, which are moving at a rate that the camera can process. If the electrospray features are moving too fast for the camera to process, a static blur is observed. In these cases, a Nanolite (High Speed Photo Systeme) flash was used to resolve the fastest moving structures of the spray. The Nanolite flash has spark durations of about 10 nano seconds. This is quick enough to freeze droplets that move up to approximately 33 ms$^{-1}$ when viewed at the maximum magnification with a resolution of 12 megapixels.
5.2 Optical Observation

The optical experimental setup allows for an observation of the electrospray at magnifications up to 1000x. The main limitation of increasing the magnification is that a blind spot begins to appear in the center of the captured images due to the focusing nature of the magnification lenses and the high luminescent light source used. For this reason an intermediate zoom was used where the picture quality was maximized and the spray details could still be seen and appreciated.

5.3 Phase Doppler Particle Analyzer (PDPA)

A Phase Doppler Particle Analyzer (PDPA) (TSI Inc.) was also used to measure various spray characteristics, such as velocity and diameter statistics. The PDPA system consists of a 2W Argon Ion Laser, a beam separator, a transmitter probe, a receiver probe, a signal processor, and computer software to operate and calibrate the system. Detailed description on the theory and principle of PDPA operation can be found in [40], however a brief overview will be given here. The system operates as follows; the beam splitter creates two pairs of laser beams. Each pair has the same wavelength but different frequencies. The transmitting probe then focuses each pair at a measurement location in front of the probe. These two beams then interfere with each other, creating fringes of light at the measurement location. However, since one of the beams is at a different frequency, these fringes are also moving in space. When a particle moves through these

Figure 5-1: Experiment schematic
fringes, it scatters the light. This scattered light is picked up by the receiver probe’s optics and directed to a photo detector. The relationship between the fringe spacing, frequency of scattering, wavelength of scattering and also the Doppler shift between signals from two consecutive fringes, allows for the calculation of particle velocity and size. One of the major advantages of using a PDPA system is its speed of measurement. Given a well calibrated system, the PDPA can make thousands of measurements per second, providing valuable statistics on the spray characteristics. Another advantage is the non-intrusiveness of measurements since the PDPA system does not alter the spray significantly. The final advantage of the PDPA system is its large measurement range. The PDPA can be calibrated to measure an extremely wide range of sizes and velocities. In order to use the PDPA system, the ground plate was modified slightly to allow the laser beams to form a measurement volume without obstruction from the ground plate. The new circular ground plate was tested by running the electrospray in all the known modes to verify that the electrical field characteristics remained unaffected.
5.4 Co-flowing air

The effect of co-flowing air on the structure and characteristics of an electrospray is one of the major investigational purposes of this work. Co-flowing air is used in practice to assist fluid breakup, enhance solvent evaporation from the droplets and also to direct the spray droplets towards the entrance of the mass spectrometer. Without co-flowing air, the droplets formed are free to move towards whichever ground surface provides the greatest electrostatic attractive force and they may simply neutralize on various surfaces around the entrance to mass spectrometer. To overcome this issue, the entrance itself is also charged to a certain potential in the order of a few hundred volts. Below is a schematic of how the co-flowing air is introduced around the electrospray nozzle:

![Figure 5-2: Electrospray nozzle and co-flow air detail](image)

As can be seen in Figure 5-2, the electrospray nozzle used in our experiments consists of two concentric stainless steel tubes. The inner tube extends out approximately 600 microns from the outer tube. The liquid is supplied via the inner tube and the co-flowing air flows around the inner tube between the inner tube outer surface and the outer tube inner surface. There is an 81 micron gap for the air flow, giving a cross sectional flow area of $9.69 \times 10^{-8} \text{ m}^2$. 


5.5 Experiment Plan

The first experiments in our lab involved using pure distilled water as a fluid. The effect of varying the electric field and liquid flowrates was observed and high speed images were captured. After these initial studies, a 50% aqueous methanol mixture was studied. Once again, the liquid flowrates and the electric field were varied. Next, a 100% Methanol solution was also studied. These initial investigations gave a better sense of how the electrospray system behaved with varying fluid properties and electric field strengths. These initial experiments also gave us the chance to optimize our optical imaging system. It was then decided to carry out a three-stage experimental plan to study the effects of co-flowing air in the electrospray. The first stage involved identifying the percentage of methanol in water that would provide the fluid properties required to achieve all regular electrospray operating modes. As identified in the literature and also from preliminary tests performed in our lab, the surface tension and conductivity of the electrospray fluid used are two of the most important parameters affecting the spraying modes achieved. With a 0 to 50% aqueous methanol solution, the steady cone-jet mode of electrospray could not be achieved. With a pure methanol solution, almost all the modes identified in the literature were observed. In actual application within a mass spectrometer, the electrospray solution used varies greatly depending on the molecules being analyzed. However, a common standard solvent mixture uses a 50% aqueous methanol solution. As an initial starting point for this study, an electrospray fluid was chosen that provided most of the previously studied operating modes, and that was similar to the solution used in practice. To satisfy this condition, a 75% aqueous methanol solution was used because as it provided all the operating modes expected and also it had similar properties to the fluids used in application. After the 75% Methanol Aqueous solution was selected, an optical study was performed using the Nanolite flash to observe the effects of adding co-flowing air while operating the electrospray in known operating modes. Finally, in order to obtain more detailed spray characteristics, a PDPA study was performed. A summary of the experimental parameters in both the optical and PDPA experiments is given in Table 13-1.

<table>
<thead>
<tr>
<th></th>
<th>Liquid Flow rate (μl/min)</th>
<th>Methanol % in Aqueous Solution</th>
<th>Air Flow rate Std ml/min</th>
<th>Air Pressure (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Optical</td>
<td>1-10</td>
<td>75</td>
<td>0-300</td>
<td>0-19.5</td>
</tr>
<tr>
<td>PDPA</td>
<td>1-1500</td>
<td>75</td>
<td>0-200</td>
<td>0-11</td>
</tr>
</tbody>
</table>

Table 5-1: Experimental Conditions for Nanolite Optical observation and PDPA analysis. The ground was 10mm from the emitter in all experiments.
6 Electrospray Characterization without Co-Flowing Air

6.1 Introduction

The following section presents results from characterizing the electrospray system at our lab. In these experiments, there was no co-flowing air applied to the emitter. This was done to generate a baseline case for our system to compare the effect of co-flowing air. Another motivation for performing a basic characterization without co-flowing air is that it adds another addition to the current experimental data on the subject and can be compared with past work. In this characterization, optical analysis was used, namely a high speed camera and a Nanolite flash.

6.2 Dripping Mode

Figure 6-1 shows the dripping mode of electrospray operation using distilled water as a fluid. With distilled water, the only modes of electrospray identified were the dripping and unstable modes. Until around 4000V, the dripping mode is present where the droplets are produced at regular intervals dictated by the balance between electrostatic, surface tension and gravitational forces. An interesting feature of this chart is present at 4000V when the droplet diameter starts to increase slightly with increased voltage. At this transition point the electrospray now begins to operate in a different mode, namely the unstable mode. In this mode the droplets no longer follow regular ejection frequencies.
Figure 6-1: Frequency and diameter of pendant water drop in dripping mode. Experiment conditions: Voltage applied at capillary tip varied from 0 V to 10,000 V; Flow rate set at 0.07 ml min−1, Ground electrode is set at 10 mm below the emitter tip. Camera Settings: 500 fps, 1/Frame seconds shutter speed.

Figure 6-2: Distilled water electrospray. Varying the voltage affects the produced drop size. Experiment conditions the same as in Figure 6-1.

In the images in Figure 6-2 it can be seen that as the electric field intensity is increased, the droplets pinching off from the capillary are reduced in diameter. However, it can also be seen that the relationship between the field strength and droplet size is not linear. Also, referring to Figure 6-1, it can be seen that the droplet production frequency and voltage is also non-linear. This nonli-
nearity could be attributed to the non-linear nature of the electric field at the capillary tip. One cause for the non-linearity of the voltage and droplet diameter relationship can be attributed to the nature of the electric field. The electric field equipotential lines are extremely dense at the emitter tip and diverge rapidly as you move towards the ground counter electrode. Since the electric field lines are non-linear in nature, it could be that as the field strength is increased, the effect on the fluid issuing from the emitter is also increasing in a nonlinear fashion. This reasoning may help to explain why the droplet size and droplet production frequency are non-linear in relationship to the applied emitter voltage.

![Diagram showing droplet sizes](image)

Figure 6-3: After a voltage of 4000, any further increase actually begins to increase the droplet size.

In Figure 6-3, another observation is that after 4000V, the droplets begin to increase in size slightly and then after a peak at about 8000V, begins to reduce. When the voltage is increased from 0 to 10000V, up to around 8000V, the droplets are ejected almost directly in the direction of the capillary axis. After 8000V, the droplets begin to drift in the radial direction to the capillary axis.
In Figure 6-5 the droplets are slightly smaller than in Figure 6-4. However, there is a significant difference in the direction that the produced droplets travel. In Figure 6-5, the droplet moves to the left and right, in relationship to the image reference, however, it seems to be ejected towards the right. One reason for this could be due to an imperfection at the capillary, such as a dust particle, or also a particle stuck in the emitter. Also, the field might have been affected by other equipment in the area.
6.3 Spindle Mode

The following figure illustrates the spindle modes as they were observed in our experiments:

![Figure 6-6: Spindle mode of electrospray operation. Approximate pulsation frequency of 500 Hz. Experiment conditions: 2500 V applied at emitter orifice, 1.2 μl/min flow rate of 75 % aqueous methanol, 10 mm ground distance from emitter. Camera: 1/250 Shutter. Nanolite flash exposure: ~12ns.](image)

As can be seen in Figure 6-6, there is a bi-modal droplet production in this mode of electrospray operation. This means that both small droplets and large droplets are produced simultaneously. In Figure 6-6A the largest droplet in the center can be seen emitting a series of smaller droplets. This type of droplet breakup is characteristic of the Coulombic fissions described in 3.2. The pulsating nature of the Taylor cone can be seen clearly in the transition between the images in Figure 6-6. Between image A and B, the cone grows towards the bottom of the image. This indicates fluid collecting in the cone between image B and C. Liquid is being ejected from the cone, and in image C it can be seen that the cone has returned back towards the emitter. In image D, it can be seen that the Taylor cone has rejected a very large jet, and in the process has become almost inverted inside the capillary. The pulsating nature of the spindle mode can be observed in the consecutive high speed camera images shown in Figure 6-7. The images in this figure show a regular pulsation of the meniscus roughly every 3ms. The camera was not able to freeze the individual jets, however, there is a multi-exposure effect that can be seen in Images A and D, which shows the residual image of either multiple jets or the same jet twisting and rotating.
6.4 Cone Jet Mode

The cone jet mode of electrospray can be extremely difficult to obtain. It requires a stable liquid flow rate, stable electric field and the right fluid properties. Once the electrospray is operating in this mode, the droplets produced are incredibly mono-dispersed. In addition to the droplets being extremely small compared with the capillary, the droplet production rate is extremely high. Using the high speed camera, it was possible to visualize, the stable Taylor cone formed in the cone jet mode, as well as in the initial jet. The breakup of the jet, however, could not be captured by the camera’s sensor due to resolution limitations. In order to study the details of the jet breakup, a Nanolite flash imaging system was employed.
As can be seen in Figure 6-8 2A to 2H, the Taylor cone is extremely stable. These images are a sample from a high speed movie that was captured. There is a 1 ms time difference between each frame. Figure 6-8 1A to1H show images of the cone jet electrospray mode taken with a high resolution DSLR camera in conjunction with a Nanolite flash. In comparison to the images in 2A-2H, the Taylor cone can be seen to move up and down slightly, modifying its cone angle. In image 1A, the cone angle is approximately ~35°, while in image 1B, this angle changes to ~23.5°. Another interesting feature observed is that the jet issuing from the Taylor cone begins to rotate and spiral slightly at the location where the droplets are produced. Image 1B shows this feature clearly. One possible effect of this rotational, spinning of the jet, is that it will induce a radial velocity component to the droplets, and hence increase the spraying cross-section.
6.5 Unstable Mode

The unstable mode of electrospray operation is extremely unpredictable, with a rich variety of phenomenon in terms of breakup mechanisms. The droplet size distribution in this mode is very wide since drops are formed due to a combination of high electric field strength, causing large drops to become ejected directly from the emitter, and also smaller droplets being emitted from unstable larger drops due to Coulombic fissions.

![Figure 6-9: Unstable mode of electrospray operation. Experiment conditions: 4000 V applied at emitter orifice, 4 μl/min flow rate of 75 % aqueous methanol, 10 mm ground distance from emitter. Camera: 1/250 Shutter. Nanolite flash exposure: ~12ns](image)

In Figure 6-9A, there is a Taylor cone emitting a large jet of liquid that seems to vary in diameter in the axial direction. The jet starts relatively small near the apex of the Taylor cone, and then expands radially in the axial direction downwards. At the end of the jet, the diameter reduces to form another miniature Taylor cone, which in itself emits two finer jets. In image B, the jet being emitted detaches as an intact jet that forms a large drop such as that seen in image C. This drop is roughly 100 microns in diameter. Even though this is a fairly small drop, considering the 300 micron emitter diameter, this is almost a magnitude larger than the smaller electrospray droplets.

In image D, the same form of a jet is seen as in image B, however, it contains a few surface disturbances. Image E could help to show how these disturbances help thin out the produced jet. In image E, the end of the jet thins out to produce small droplets through Coulombic fissions.
Figure 6-10: Unstable mode of electrospray operation. Experiment conditions: 100 microliters/min of 50% Aqueous Methanol. High Speed Camera Images with 2ms between consecutive images. Ground was 4.18 mm below emitter.

Figure 6-9 shows Nanolite flash images of the unstable mode. Since these images are not captured chronologically, it is difficult to observe how droplet formation is taking place from one
image to the next, because there is no continuity. By contrast, Figure 6-10 shows high speed camera images in sequential order. Having the images laid out in this manner helps us to better understand the repeating patterns and mechanisms involved in the spray. Image 1A in Figure 6-10 shows a jet being emitted with two large varicose surface wave peaks. In image 1B, the evolution of these two surface wave’s results in the formation of two droplets. The droplet sizes are around 50 microns in diameter. In Image 1C and 1D, a similar evolution of droplets takes place. However, there is a further breakup of the droplet at the bottom of the image in Image 1D. The second drop then also goes through a secondary breakup, as shown in Image 1E. In this image, the droplet can be seen forming a Taylor cone and emitting a stream of smaller drops. For the complete sequence of images for the 3500V condition in Figure 6-10, one interesting feature is that all the produced jets and droplets have a radial component of movement, namely to the right of the image. This directional feature was also observed in Figure 6-5, where an electrospray with distilled water was operating in the unstable mode. In Figure 6-10, Image 1A, all the large droplets emit secondary jets. There appears to be a higher rate of drop production for the 4000V case than the 3500V case. In the 4900V, there seems to be minimum droplet production as there are three images with no droplets being produced at all. It seems as though, due to the higher electric field strength, all the liquid gets ejected, as one jet, and the capillary then sits empty for a moment until more liquid accumulates. Using an even higher frame rate on the high-speed camera, the breakup of the large jets in the unstable mode was captured in detail as shown in Figure 6-11.

![Figure 6-11: Unstable mode of electrospray. Experiment conditions: 4000V, 70 microliters/min of 50% aqueous methanol solution, 10mm ground distance. High speed camera at 1000 fps.](image-url)
6.6 Electrospray Operating Modes

One of the main results from the electrospray characterization without air was that an operating mode chart could be developed. This type of chart shows the electrospray operating modes for our particular electrospray system for a given fluid. Figure 6-12 shows the operating chart for a 75% aqueous methanol solution electrospray in our system.

![75% Aqueous Methanol Operating Chart](image)

Figure 6-12: Operating modes for a 75% Methanol Aqueous Solution. Ground distance was set to 10mm.

Using 75% aqueous methanol as a solution, you will obtain different electrospray operating modes dependant on the selected liquid flow rate and voltage applied to the emitter. For example, at a flow rates of 5 microliters/min, from 0 to approximately 2400V, you should observe the dripping mode of electrospray operation with increasing droplet production frequency and reducing droplet diameter with increased voltage. From around 2400V until around 3200V you will now see the spindle mode of electrospray operation. From 3200V till around 3600V, you will establish the cone jet mode. Any further increase from 3600V will take you into the unstable modes of operation. From the operating chart of the 75% aqueous methanol solution shown in Figure 6-12, it is clear that below a liquid flow rate of approximately 11 µlmin⁻¹, all the regular modes of electrospray are observed. For all later experimental stages, the range of flow rates from 0 to 10 microliters/min is used to capture these modes. With the use of 50% aqueous methanol, it was not possible to obtain the cone-jet mode of electrospray. In this case, the electrospray transi-
tioned from dripping to spindle and then to the unstable mode. In order to see the effects of co-
flowing air on as many different electrospray modes as possible, including the cone jet mode, the
75% aqueous solution was used.

6.7 Electrospray Solution Freshness

The solution used in our experiments consisted of a methanol and distilled water mixture. As
shown in the discussion in 6.6, the percentage of the methanol in the distilled water is an ex-
tremely important parameter. It was determined that the solution mixture should be used as soon
as it is created, since there is a rapid evaporation of the methanol from the mixture, changing the
percentage of methanol in distilled water. If the solution was left for too long in the syringe the
operating modes would be modified. To keep the experiments consistent, all solutions were used
within 10-15 minutes of being prepared. To confirm that this timeframe is sufficiently short to
not affect the electrospray, a few different flow rates were scanned twice from 0 to 10000 volts,
of a 75% aqueous methanol solution. These two scans were performed at two times 30 minutes
apart. There was no observable difference in the electrospray operating mode chart as compared
with Figure 6-12.
6.8 Jet Breakup

The instability and breakup of a liquid jet is important to many processes such as particle production, fuel injection and mass spectrometry. The first investigation of jet instability was performed by Rayleigh using small perturbation theory to study under what conditions did disturbances grow or decay on the surface of an inviscid cylindrical jet in air [12]. These studies were later extended to include the effects of viscosity, charge and also other surrounding fluids [41][42][43]. The main result from these studies was an understanding, based on the physics of the problem, of which wavelengths of disturbances would cause a growth of instabilities on the surface of the jet and also whether jet properties and conditions such as charge and viscosities would enhance or dampen these instabilities. In this section the jet breakup in the cone-jet mode will be discussed based on experimentally measured data as well as an analytical analysis.

6.8.1 Optical Analysis Using Imaging Software

![Image A](image1.png) ![Image B](image2.png) ![Image C](image3.png)

Figure 6-13: Cone-jet mode of electrospray operation. Experiment conditions: 4 µl min⁻¹ flow rate of 75% Methanol Aqueous Solution, 3400 V, 10mm ground distance.

In Figure 6-13A, the image uses a high speed camera system with a constant light source and a 500 µs shutter speed. The resulting image is that of a Taylor cone formed at the emitter and a jet coming out of the apex of the cone. Due to the speed of the droplets formed from the jet, the 500 µs shutter speed is insufficient to freeze the droplets. Figure 6-13B, in the center shows the same mode of electrospray as in Figure 6-13A. However in this case, the 0.012µs exposure of a Nano-
Lite flash is fast enough to effectively freeze the droplets formed from the jet. Figure 6-13C is a section of Figure 6-13B that has been modified in an image analysis program ImageJ [44]. This image has been analyzed in the following way. A Sobel edge detection algorithm calculates the gradient, or rate of change, of intensity at each point in the image. It then highlights the areas where this is the highest. This system provides a good way to detect drop and jet boundaries. After this the image is converted to a binary image using the detected edges. After converting the image to binary, there may still be a few areas, especially within the drops themselves due to light refraction, which are not converted to binary properly. These areas are filled in with another algorithm designed specifically for this task. At this stage, it is now possible to measure the area of each droplet automatically and hence estimate its diameter, assuming it is sufficiently spherical.

Figure 6-14: Images being processed for droplet size and jet measurement.

One of the main issues with using image analysis is that the results are highly dependent on the image contrast. This is clearly illustrated in Figure 6-14-A and B. In image A1, the contrast is not as consistent as in B1. This resulted in the edge detection algorithm not detecting nine drops. In comparison, in image B1, the software detected all the drops present. Another issue is that the edge detection algorithm overestimates sizes, since it applies a boundary of a few pixels thick around each drop. This effect is dependant once again on the contrast and hence, a high contrast in the original image is critical. As discussed, slight change in contrast can modify the measured edges and thus size measurements. This error is amplified if you are measuring distances that are in the order of a few pixel lengths. To account for measurement variations, all the image analysis performed is done using the same procedure and settings in terms of applying edge detection and
converting to binary. This helps to minimize variation between measurements improving the accuracy of the results. The diameter of the jet can be measured directly at various points to obtain an average and the breakup wavelengths can also be measured in a similar manner. The breakup length and jet diameter measurements were performed manually after performing image enhancing algorithms. The reason for manually calculating the breakup lengths and jet diameter was because no algorithm existed to do this since it is more complex than calculating drop area. An algorithm could be developed in the future, however, due to time limitations, these dimensions were measured manually. To calculate the error in these manual measurements, multiple measurements of the same image were made in a row. The measurements were then analyzed and a standard deviation calculated. This error has been calculated as 0.5µm, or approximately 3-4% of the breakup wavelength value. A plot of the measured breakup wavelengths as compared with predicted wavelengths based on the jet diameter is given in Figure 6-15.

\[ \lambda = \frac{\pi D_j}{0.697} \]  \hspace{1cm} (6-1)

Figure 6-15: The breakup wavelength of the jet in the cone jet mode of Electrospray operation.

Rayleigh solved the dispersion equation for an unstable jet [12] yielding the following relationship:
Where $\lambda$ is the breakup length (m) and $D_j$ is the jet diameter. The calculated linear line in Figure 6-15 is based on this relationship and also the measured jet diameter. As can be seen in Figure 6-15, the measured breakup wavelengths for a charged jet in our experiments follow the same trend as that for an uncharged jet. However, it should be noted that most of the data points are below the calculated line. This could be an indication that the charge has a minor effect. Further investigation is required to verify this. In fact, previous authors have also found that the charge affects the relationship between breakup wavelength and jet diameter. In Basset’s work [42], he concludes that for jet circumference ratios to disturbance wavelength bigger than 0.6, the charge tends to produce stability, and for ratios below this the charge causes instability. This ratio translates to a slope of 5.23. In the experimental data shown in Figure 6-15, we see that the calculated slope is close to that of an uncharged jet, which is approximately 4.55. This indicates that according to Basset’s analysis, our jet is breaking up in a manner where the charge is actually producing stability. However, due to the errors in measurement in Figure 6-15, this needs to be verified through further experimental work. This analysis shows that the charge of the jet has a negligible effect on the jet breakup mechanism in the case of our experiments and that the breakup is similar to that of an uncharged jet. The ratio between the unstable jet and drops produced can be related as shown the following relationship [10]:

$$\frac{D_d}{D_j} = 1.89 \quad (6-2)$$

The above relationship has been shown to hold for uncharged jets and as can be seen in the following plot, out experimentally measured values of charged jet and drop diameters also appear to follow this relationship:
As seen in Figure 6-16, for a charged jet producing droplets, due to Rayleigh instabilities, the drop-to-jet diameters generally follow the same relationship as an uncharged jet. However, in our experiments, we observe that all the measured points fall under the calculated value for an uncharged jet. This again indicates that the charge has a slight effect on droplet size that is not captured in the original analysis of an uncharged jet.

### 6.8.2 Charged Jet Instability Analysis

The preceding section concluded that a charged jet breaks up in a similar manner to an uncharged jet. The following section will now look at the analytical solution to the dispersion equations for a charged liquid jet. The methods used to derive the dispersion equations follow previous work in which the mechanical energy balance method was used [43]. This method uses fundamental energy relationships applied to a fixed control volume to arrive at the same dispersion equation as initially derived by Rayleigh, based on the Lagrangian motion of the jet.
6.8.2.1 Instability Analysis

The basic methods used to derive the dispersion equation are briefly presented here. First, consider the mechanical energy balance for a fixed control volume of fluid.

The balance for the mechanical energy of the control volume in Figure 6-17 can be written as:

\[1. \int_S \frac{1}{2} \rho q^2 u_j n_j dS + 2. \int_v \frac{\partial}{\partial t} \frac{1}{2} \rho q^2 dV - 3. \int_S Pu_j n_j dS = 0 \quad (6-3)\]

Equation (6-3) is the integral relationship used to derive the Rayleigh dispersion equation of a liquid jet. Working in cylindrical coordinates, the following figure shows the geometry of the jet in question:
In Figure 6-19, “a” is the undisturbed jet radius, α is the amplitude of disturbance, \( r_s \) is the radius of the disturbed jet and \( \lambda \) is the wavelength of the disturbance. Also \( r_s \) is described as:

\[
r_s = a + \alpha \cos k z \tag{6-4}
\]

In equation (6-4), \( k \) is the wave number of the perturbation defined as \( \frac{2\pi}{\lambda} \). For this analysis the flow is considered irrotational, therefore we can define a velocity potential function that consists of two superimposed components, one for the undisturbed flow field and another component for the perturbed flow field.

\[
\phi = \phi_o + \phi' \tag{6-5}
\]

The undisturbed flow field is simply a uniform flow in the \( z \) direction, while the flow field for the perturbed flow is yet to be determined. However, it is assumed to be a function of \( r \) and \( z \) only and therefore we can use the separation of variables technique to represent it.

\[
\phi' = f(r) x(z) \tag{6-6}
\]

The perturbed potential function in equation (6-6) must satisfy Laplace’s equation:

\[
\frac{1}{r} \frac{\partial}{\partial r} \left( r \frac{\partial \phi'}{\partial r} \right) + \frac{\partial^2 \phi'}{\partial z^2} = 0 \tag{6-7}
\]

\[
\frac{1}{rf(r)} \frac{\partial}{\partial r} \left( rf(r) \frac{\partial f(r)}{\partial r} \right) + \frac{1}{x(z)} \frac{\partial^2 x(z)}{\partial z^2} = 0 \tag{6-8}
\]

From equation (6-8), it is determined that the solution for the function \( f(r) \) is the modified Bessel function \( I_0(kr) \) and the solution of the function \( x(z) \) is \( \cos(kz) \). Therefore, the complete velocity potential for the problem can be written as:

\[
\phi = w_0 z + \beta I_0(kr) \cos kz \tag{6-9}
\]
Where in equation (6-9), the constant uniform velocity of the jet is $w_0$ and $\beta$ is a constant to be determined. To evaluate the constant $\beta$, the radial velocity at the jet surface is determined using equations (6-4) and (6-9). This gives:

$$\beta = \frac{\dot{\alpha}}{kI_1(ka)}$$  \hspace{1cm} (6-10)

Combining equations (6-9) and (6-10) yields the complete velocity potential for the problem at hand:

$$\phi = w_0 z + \frac{\dot{\alpha}}{kI_1(ka)} l_0(kr) \cos k z$$  \hspace{1cm} (6-11)

In order to evaluate the integrals in (6-3) we need to obtain an expression for the pressure at the surface. This is done by using the Young – Laplace equation which yields the following:

$$P = \frac{\gamma}{a} - \frac{\alpha \gamma}{a^2} (1 - k^2 a^2) \cos k z$$  \hspace{1cm} (6-12)

Using the relationship for pressure in equation (6-12), the velocity potential in equation (6-11) and identities for the modified Bessel functions, the integrals in equation 1 are evaluated as follows:

$$\int_s \frac{1}{2} \rho q^2 u_j n_j dS = 0$$  \hspace{1cm} (6-13)

$$\int_v \frac{\partial}{\partial t} \frac{1}{2} \rho q^2 dV = \frac{\dot{\alpha} \alpha 2 \pi^2 n \rho a I_0(ka)}{k^2 I_1(ka)}$$  \hspace{1cm} (6-14)

$$\int_s P u_j n_j dS = \frac{\dot{\alpha} \alpha 2 \pi^2 n \gamma}{ka} (1 - k^2 a^2)$$  \hspace{1cm} (6-15)

After combining equations (6-13)(6-14) and (6-15) in 1 and simplifying, the final differential equation for the motion of an inviscid perturbed cylindrical jet becomes:

$$\ddot{\alpha} = \alpha \frac{\gamma}{\rho a^3} \left[ \eta (1 - \eta^2) \frac{I_1(\eta)}{I_0(\eta)} \right]$$  \hspace{1cm} (6-16)
Where in equation (6-16) \( \eta = ka \). Equation (6-16) is a second order ODE with solutions of the following form:

\[
\alpha = Ae^{\omega t} \tag{6-17}
\]

Solving for the frequency \( \omega \) in equation 15 we get:

\[
\omega^2 = \frac{Y}{\rho a^3} \left[ \eta (1 - \eta^2) \frac{I_1(\eta)}{I_0(\eta)} \right] \tag{6-18}
\]

Equation (6-18) describes the conditions for when the disturbances applied to the liquid jet will grow or just cause a periodic oscillation of the jet surface in the radial direction. If \( \omega \) is imaginary, the oscillations will oscillate with time and the jet is stable. If \( \omega \) is positive, the oscillations will grow exponentially in time, causing the jet to be unstable. The term that determines whether \( \omega \) is imaginary or positive is \((1 - \eta^2)\) or \((1 - ka^2)\). If \( ka \) is greater than 1, then \((1 - ka^2)\) evaluates to a negative number and hence \( \omega \) would be imaginary, producing a stable oscillation. If, however, \( ka \) is less than 1, then \((1 - ka^2)\) evaluates to a positive number and hence \( \omega \) is also positive. In this case, oscillation will grow exponentially causing jet breakup. Since \( k \) is \( \frac{2\pi}{\lambda} \) this leads to the following conclusions:

\[
\text{If } \lambda < 2\pi a \text{ the jet is stable} \tag{6-19}
\]

\[
\text{If } \lambda > 2\pi a \text{ the jet is unstable} \tag{6-20}
\]

Equation (6-19) states that the jet is stable for disturbance wavelengths that are smaller than the circumference of the unperturbed jet. Equation (6-20) states that for disturbance wavelengths that are greater than the circumference of the unperturbed jet, the jet is unstable. The effect of surface tension on the stability of the jet can also be deduced from equation (6-18). Intuitively, the larger the surface tension, the more of a pinching effect this has on the jet curvature and therefore, we expect that the jet would become unstable more quickly. This is seen easily in equation (6-18) as a higher surface tension value would yield a higher frequency \( \omega \) for the same applied perturbation and hence, the disturbance would grow quicker with time. This is illustrated in the following figure:
The numerical plot of the solutions to the dispersion equation (6-18) can be seen in Figure 6-19. The maximum growth rate for $\omega$ is approximately when $ka = 0.697$. This result is the same as derived by Rayleigh and it can be seen that increasing the surface tension has no effect on the wavelength for the maximum growth rate but only on the magnitude of the growth frequency $\omega$.

### 6.8.2.2 Viscosity

Next, the effect of viscosity on the previous instability analysis will be taken into account. The analysis is performed in an identical manner to the inviscid jet; however there is an extra term in the mechanical energy balance equation that accounts for viscous energy dissipation:

$$
\int_s \frac{1}{2} \rho q^2 u_j n_j dS + \int_v \frac{\partial}{\partial t} \frac{1}{2} \rho q^2 dV - 3 \int_s Pu_j n_j dS + 4 \int_v R dV = 0 \quad (6-21)
$$

Where $R$ is:

$$
R = \frac{\mu}{2} (u_{i,j} + u_{j,i})(u_{i,j} + u_{j,i}) \quad (6-22)
$$
The effect of viscosity is expected to dampen the oscillations of the jet and therefore promote stability. The integrals 1, 2 and 3 in equation (6-21) are evaluated to get the same results as before, and the 4th integral is evaluated to be:

\[
\int_v RdV = \frac{n\pi^2}{2k}(24 + k^2a^2) \tag{6-23}
\]

Where the following approximation has been used which is valid for \(\eta < 1\):

\[
\frac{l_4(\eta)}{l_0(\eta)} = \frac{\eta}{2} \tag{6-24}
\]

Thus combining the integral results from equations (6-22), (6-13), (6-14), (6-15) with equation (6-21) and using the approximation in equation (6-23), we get the following differential equation for the motion of a viscous perturbed cylindrical jet:

\[
\ddot{\alpha} + \frac{\mu k^2}{\rho} \left(\frac{24 + \eta^2}{8 + \eta^2}\right) \dot{\alpha} - \frac{4\gamma\eta^2(1 - \eta^2)}{\rho a^3 \left(8 + \eta^2\right)} \alpha = 0 \tag{6-25}
\]

The solutions of equation (6-24) are of the same form in equation (6-17), therefore solving for the frequency \(\omega\) we have:

\[
\omega^2 + \frac{3\mu k^2}{\rho} \omega - \frac{\gamma}{2\rho a^3}(1 - \eta^2)\eta^2 = 0 \tag{6-26}
\]

Using the quadratic formula we can better visualize the effect viscosity has on the nature of the frequency solutions:

\[
\omega = \frac{-3\mu k^2}{2\rho} \pm \sqrt{\left(\frac{3\mu k^2}{2\rho}\right)^2 + \frac{\gamma}{2\rho a^3}(1 - \eta^2)\eta^2} \tag{6-27}
\]

As can be seen from equation (6-26), the instability region for the jet is for values of \(\eta\) between 0 and 1. This translates to disturbance of wavelengths that are bigger than the circumference of the unperturbed jet. This indicates that effect of viscosity doesn’t change the general nature of
the instability solution. However, it does dampen and reduce the growth frequency and thus promotes stability. This is visualized in the following figure:

Figure 6-20: Effect of viscosity on jet instability

The numerical plot in Figure 6-20 shows curves for $\omega$ labeled from 0 to 3 in order of increasing viscosity. This clearly shows that viscosity has a stabilizing effect on jet instability.

6.8.2.3 Charge

The effect of charge will now be added to the instability analysis. The resulting differential equation will then be analyzed by isolating the effect of charge on jet instability. The first assumption that needs to be made in regards to a charged jet, is that the jet is sufficiently conducting so that all charge lies on the surface. The effect of surface charge on the jet surface would be to create an electric pressure in the outward direction that opposes the surface tension force. This means that equation (6-12), for the pressure at the jet surface, needs to be modified by adding this extra electric pressure term:

$$P = \frac{\gamma}{a} - \frac{\alpha \gamma}{a^2} (1 - k^2 a^2) \cos kz - F_{EP}$$  \hspace{1cm} (6-28)
Where:

\[ F_{EP} = \frac{\sigma_0^2}{2\varepsilon_0} \left( 1 - \frac{2\alpha}{a} \cos kz \right) \]  \hspace{1cm} (6-29)

In equation (6-29), \( \sigma_0 \) is the surface charge density of the jet and \( \varepsilon_0 \) is the permittivity of free space. If we review the integrals in equation (6-21), the effect of adding charge and modifying the pressure relationship at the jet surface only affects the 3rd integral. This integral then evaluates as follows:

\[ \int_S P u_j n_j dS = \frac{2n\pi^2 \gamma \dot{\alpha} \alpha}{k} (1 - k^2 a^2) - 2n\pi^2 \frac{\sigma_0^2}{\varepsilon_0 k} \dot{\alpha} \alpha \]  \hspace{1cm} (6-30)

To obtain the instability equation for a viscous charged jet, we can now combine equations (6-22), (6-13), (6-14), and (6-29) with equation (6-21) and use the approximation from equation (6-23) to get:

\[ \ddot{\alpha} + \frac{\mu k^2}{\rho} \left( \frac{24 + \eta^2}{8 + \eta^2} \right) \dot{\alpha} - \left[ \frac{4\gamma \eta^2 (1 - \eta^2)}{\rho a^3 (8 + \eta^2)} - \frac{4\sigma_0^2 \eta^2}{\varepsilon_0 \rho a^2 (8 + \eta^2)} \right] \alpha = 0 \]  \hspace{1cm} (6-31)

Once again, the solutions to this ODE are of the form shown in equation (6-17) and the corresponding dispersion frequency equation is:

\[ \omega^2 + \frac{3\mu k^2}{\rho} \omega - \left[ \frac{\gamma}{2\rho a^3 (1 - \eta^2) \eta^2} - \frac{\sigma_0^2 \eta^2}{2\varepsilon_0 \rho a^2} \right] = 0 \]  \hspace{1cm} (6-32)

Equation (6-31) can now be solved using the quadratic equation and this also helps to visualize the effect of charge on the stability of the jet:

\[ \omega = -\frac{3\mu k^2}{2\rho} + \sqrt{\left( \frac{3\mu k^2}{2\rho} \right)^2 + \left[ \frac{\gamma}{2\rho a^3 (1 - \eta^2) \eta^2} - \frac{\sigma_0^2 \eta^2}{2\varepsilon_0 \rho a^2} \right]} \]  \hspace{1cm} (6-33)

If we keep the viscosity and surface tension effect constant, the effect of increasing the charge can be seen in the following figure:
As can be seen in Figure 6-21, the effect of increasing the charge tends to produce jet stability by lowering the instability frequency magnitude and also lowering the range of disturbance wavelengths that are unstable in the first place.

6.8.3 Conclusions

The instability analysis of an inviscid jet was performed. The numerical plot of the solution revealed, as expected, that increasing surface tension of the fluid increases jet instability due to the increase in pinching action. Next, the effect of viscosity was considered and added into the analysis as a viscous dissipation term. The effect of viscosity was to dampen any oscillations and hence produce stability. This was also observed in the numerical plot of the solution for a viscous jet. Finally, we added the effect of charge to the jet, where it was assumed that the jet is sufficiently conducting so that all charge is at the surface. With this assumption in place, we can introduce an electric pressure at the jet surface in the outward direction, which opposes the surface tension pinching pressure. This was also shown to produce a stabilizing effect that was also observed through the numerical plot of the solution. An additional effect was also seen, the effect of reducing the range of wavelengths that cause instability in the first place.
The numerical analysis combined with the optical analysis concludes that a charged jet will breakup in the same manner as an un-charged jet. The main jet breakup wavelength also remains unchanged, as is shown by various experimental measurements as well as the well known dispersion relationship which Rayleigh initially solved. An interesting effect of the charge was revealed in the numerical analysis, where, although the wavelength at which the jet breakup takes place remains unchanged, the range of wavelengths that cause instability reduces. This indicates a stabilization effect of the charge. However, one very important variable is missing from the above analysis when applied to an electrospray system, and that is the electric field. The electric field will interact with the jet in a very complex manner and is not included in the preceding numerical analysis. There has, however, been a significant amount of work on this area of jet breakup concluding that a charged jet produces droplets of a smaller size than an uncharged jet. Most of the experiments performed in these previous studies [45][46], however, consisted of jets that were much larger in diameter compared with those measured in this work. They were on the order of two magnitudes larger. This could also be a reason why the charge has little effect on initial jet breakup in the cone jet mode in our experiments.
7 Electrospray Characterization with Co-Flowing Air

7.1 Co-Flow Air Flowrates

After completing the electrospray characterization without co-flowing air, co-flowing air was then introduced at varying air flowrates. The air flowrates were chosen such that the electrospray modes were still visible for optical analysis. It was found that above a flow rate of 300 std ml/min of air, there was no observable spray features at the emitter tip. This could be due to the high air velocities above this flow rate. Our imaging system has a resolution of 0.35 microns/pixel and the Nanolite flash duration is approximately 12 nanoseconds. This means that our images can capture spray features moving slower than 29 m/s. anything moving quicker than this speed would result in blurred images, which was the case at higher air flowrates. Based on the annular air flow area, and air flow rate, the speed of the air exiting the emitter is shown in Figure 7-1.

![Co-Flow Air Flow Rate vs. Estimated Air Velocity at Emitter](image_url)

Figure 7-1: Estimated air velocity at emitter tip vs. Air flow rate. Calculations are based on air pressure in the delivery system.

7.2 Spindle Mode

The following section describes the effect of nebulizing air on the spindle mode of operation.
Figure 7-2: Spindle mode of electrospray operation. Experiment conditions: 4 microliter/min flow rate of 75% aqueous methanol solution, between 2200 and 3400 V applied to the emitter tip, 10mm ground distance. All images taken with a Nanolite flash.
In Figure 7-2, it can be seen that as co-flowing air is added, the droplets being formed are bound by the co-flowing gas pressure around the emitter. This effect is observed in images 4A and 5D. In 4A, the jet that has been emitted from the capillary, whips in a wide wavelike structure. In image 5D, the jet can be seen to not whip to such an extent as in image 4A, and also it can be seen that all the droplets being produced are being bound inwards by the co-flowing air. Even at a relatively low air flow rate, such as in image B1, the produced droplets can be seen to stay together in contrast to the way the droplets immediately begin spreading out at the bottom of image A5. The estimated air velocities are significantly higher than the estimated spindle mode droplet velocities. Therefore, there will be a shearing type interaction between the two fluids, causing the droplets to accelerate in the direction of the airflow. Between Figure 7-2 A and Figure 7-2 B, there is no significant difference apart from the direction of the spray structure. The spray is directed slightly to the left in the image which is also the case in Figure 7-2 C and Figure 7-2D, where the air flow rates are much higher. The reason for the co-flowing air to consistently direct the spray structure to one direction, relative to the nozzle, needs to be investigated further because it could either be a nozzle imperfection or a feature of the air flow due to the way it is introduced into the co-flowing capillary.
7.3 Cone Jet Mode

Figure 7-3: Cone jet mode of electrospray operation with varying co-flowing air flow rates. Experiment conditions: 3200V applied at emitter, 75% aqueous methanol supplied at 2.4 microliters/min.
In Figure 7-3, the image sets A, B, C and D show the effect of co-flowing air on the cone jet mode. In image set D, we see an interesting version of the cone jet mode, where a stable spiral has formed. The co-flowing air seems to be a factor in the spiraling effect of the cone jet. One of the reasons why co-flowing air could be a factor is that it is introduced perpendicularly to the direction of the liquid flow, as shown in Figure 7-6. Using co-flowing air and at a slightly higher liquid flow rate, it is observed that the spiraling jet was not formed. This could be because the higher hydrostatic pressure in the cone jet overcomes the influence of the co-flowing air. There is, however, still an observable shift in the jet direction with the addition of co-flowing air. This is shown in Figure 7-4.

Figure 7-4: Cone jet mode of electrospray operation with varying co-flowing air flow rates. Experiment conditions: 3200V applied at emitter, 75% aqueous methanol supplied at 5 microliters/min.
Figure 7-5: Cone jet off-axis angle vs. co-flowing air flow rate. Experiment conditions: 3200V applied at emitter, 75% aqueous methanol supplied at 5 microliters/min.

As shown in Figure 7-4 and Figure 7-5, the addition of co-flowing air has a significant effect on the off-axis angle of the cone jet.

Figure 7-6: Nebulization Air Introduction Location and Direction

As seen in Figure 7-6, the way that the co-flowing air is introduced into the capillary could be a reason why the co-flowing air tends to consistently push the liquid jets emitting from the capillary to one side or in some cases, such as in the cone jet mode, to cause the liquid jet to spiral.
The co-flowing air is injected perpendicularly to the axis of the emitter, about 200 mm before the exit of the electrospray emitter. This point is labeled point 1 in Figure 7-6. Since the air is being injected relatively early into the plumbing system compared with the piping and tubing diameters, the initial turbulences at point 1 should not have a significant effect on the airflow at the outlet, labeled point 3. However, as can be seen in Figure 7-3 image set D, the cone jet formed seems to be following a spiral shape which could be attributed to this perpendicular injection of air. Another region that may play an important part in the development and delivery of the co-flowing air is the pneumatic connection between the electrospray’s main housing and the emitter housing. This is shown as point 2 in Figure 7-6. This connection contains an orifice plate that connects the co-flowing air from the main housing to the emitter body. There may be a pressure build up at this orifice plate and, therefore, a turbulent flow induced afterwards. Another feature of the co-flowing air delivery system is the fact that it involves the positioning of two concentric tubes. If there is a slight eccentricity in the tube positioning, it may cause an asymmetric flow at the emitter outlet. To verify this, a magnified high resolution image of the emitter outlet is taken, shown in Figure 7-7.

![Figure 7-7: Magnified image of the emitter tip showing the measured co-flow air gaps on either side.](image)

Figure 7-7 shows that the fluid capillary is approximately 35% off-axis, and is not concentric with the co-flowing air housing. This eccentricity in positioning can cause a non-symmetric effect on electrospray jets and droplets produced.
7.4 Unstable Mode

In the unstable mode of cone jet operation, the spray operates in a completely unpredictable manner. Due to this unpredictability, it was extremely difficult to observe the electrospray in this mode. The high speed camera analysis in section 6.5 showed that in the unstable mode, the liquid at the emitter tends to get ejected as one big bulk liquid jet, which eventually forms large droplets. In Figure 7-8, this same type of electrospray behavior can be seen. Images A1, A2 and A4 all show a jet beginning to emerge from the meniscus. In image A3, a jet has already been emitted and the meniscus can be seen returning to a hemispherical shape because the bulk charges that caused the Taylor cone shape to be formed have simply been emitted within the jet. Image B1 in Figure 7-8 shows the co-flowing air assisting in jet break-up. The droplets formed are not allowed to spread radially due to the air pressure around the jet. It should be noted that there are no Nanolite flash images in the 100 Std ml/min co-flowing air case. This was due to not being able to capture any satisfactory images during the experiments. Even when there is no co-flowing air applied to the system, it is difficult to capture jets being emitted in the unstable mode, due to the inconsistency with which these ejections happen. With the addition of air, the jet tends to move even faster, making it even more difficult to capture. In contrast, in the spindle and cone jet modes, the electrospray is highly repeatable. This makes it possible to capture different sections of a particular type of phenomenon from images taken at various times, and to be able to piece them together to explain some of the processes involved. In the case of the instable mode, however, this was extremely difficult.
7.5 PDPA Study – 75% Aqueous Solutions

7.5.1 Single Point Analysis

To determine proper measurement locations for the PDPA system, the following procedure was employed. First, the measurement volume was focused just below the emitter tip. Then, liquid was supplied to the emitter at a flow rate high enough so a jet was formed from the hydrostatic pressure. There was no charge applied because we wanted the jet to flow vertically from the emitter. Once the measurement location on the jet was centered, the cone jet mode of operation was established. Then the PDPA system was used to gather measurements. Close to the Taylor cone, the droplets formed were extremely close together, giving a low data rate on the PDPA system. By moving the measurement volume away from the emitter in the direction of the spray axis, better data rates were recorded when the droplets spread out radially enough that valid measurements could be made. The above procedure was repeated for the spindle mode. All PDPA measurements were made at a distance of 1.87 mm below the emitter tip in the axial direction to the emitter’s housing.

Initially, we decided to make measurements at a single point, 1.87 mm below the emitter, for all conditions. There were a few issues with this approach. One issue was that because the spray was so small, when the spray was slightly non-symmetric and pointed away from the vertical normal to the emitter, then the measurements made would be different for similar cases made at different times. This is verified in the preceding optical analysis section because the jet can spray in various directions, depending on the nature of the electric field and also the nature of the co-flow of air around the emitter. Another issue with making measurements at a single point is that the electrospays can be highly poly-dispersed and, therefore, there will be a bias if measurements are made at only one point in the spray. The initial motivation for making only a single point measurement for each case was the fact that it would be less time-intensive than multiple measurements and many different conditions could be studied. However, due to time limitations, another approach was taken.

7.5.2 X-Y Planar and Linear Analysis

To obtain a more meaningful data set that can be used to compare the various conditions for our electrospay system, we chose to perform a complete X-Y planar scan at a fixed Z distance of
1.87 mm. The X-Y scan was performed for two operating modes; the spindle and cone jet modes. In these two modes, the spray behaves in a relatively repeatable manner, so meaningful measurements could be made. In both these modes, two scans were performed; one without any co-flowing air and one with 200 Std ml/min of co-flowing air. PDPA analysis was also performed on various unstable modes of electrospray operation, where the spray behaves in an unpredictable manner. In these cases, the data rates were extremely low, so instead of a complete X-Y scan, a single linear scan along the X axis was performed. The following section presents the main results from the PDPA analysis and relevant discussions. In all cases, a 75% methanol aqueous solution was used, the ground distance was set to 10 mm, and the measurements were made 1.87 mm below the emitter tip.

For each of the Electrospray modes tested, the spray ensemble averages for diameter and velocity are given in the following figures. The planar scan of the PDPA provided droplet measurements of the entire cross-section of the spray with a resolution of 100 microns between points. At each point, the data rate can be defined as the number of valid measurements per unit time. This value fluctuated between all measured points, depending on spray characteristics at each one. Where there are higher data rates, the PDPA system would take thousands of measurements within a few seconds, and at a region of low data rate, only a few drops were measured within a minute. If we simply average all the droplets, the lower data rate measurements would skew the average. To obtain a more representative average of the entire spray area, the measurements made at each point were weighted by their data rate.
7.5.3 PDPA Data Collection Method

At each measured point in the spray, the PDPA system collected data until 20,000 validated measurements for velocities and diameter were obtained. For example, in the case of the spindle mode, there were 245 measurement locations yielding a total of 4,900,000 individual measurements. In some cases, the valid data rates were extremely low so it was not practical to leave the system running due to time limitations. Also, these low data rates were usually during the unstable modes of electrospray operation and, therefore, the average results in these modes are not as well represented as in the spindle or cone-jet modes.

In the cone-jet mode, the entire electrospray cross-sectional scan was performed twice to ensure reliability. The measurements were performed initially and then the entire system was turned off and restarted the following day. This data is shown in Figure 7-9. From looking at the data in Figure 7-9, all the plots and histograms are very similar with two main differences. One difference is in the axial velocity histogram as well as the axial velocity vs. diameter plot. The axial velocity histogram plot shows that on the following day, the entire distribution shifts upwards. From the axial velocity vs. diameter plot, we see that there are almost no droplets moving slower than 5 m/s on the second day as compared with many on the first day. Another difference can be seen in the radial velocity histogram. The two histograms between the first and second day are almost mirror images of each other about the y axis. In the first day, the distribution is weighted towards the positive side, and on the second day it is towards the negative side.
Figure 7-9: Cone jet mode PDPA data verification. Experiment conditions: 7 microliter/min flow rate of 75% aqueous methanol.
The diameter results in Figure 7-10 show that co-flowing air causes a slight increase in droplet size for the spindle and cone-jet modes. Referring to the optical study that preceded the PDPA analysis, the addition of co-flowing air did not show any affects that would cause the electro-spray to produce larger droplets in the spindle and cone-jet modes. However, in both the spindle and cone-jet mode, a shift in spray direction was observed along with a co-flowing air bounding
effect that keeps the spray droplets together once they are formed. In the unstable mode, the droplet size decreases marginally with the addition of co-flowing air. Also, in the high flow rate unstable mode, the addition of co-flowing air seems to have no real effect on droplet size. At this point it is important to look at another spray characteristic, the axial velocity of the droplets. The axial velocity of the droplets is given in Figure 9. Looking at the velocity data in Figure 7-10, the first major observation is that all the electrospray modes, except the cone-jet mode, are influenced by the co-flowing air. In the cone-jet mode, both the droplet diameter and velocities are minimally affected. For the spindle mode and unstable modes, the axial velocities are significantly affected with the addition of co-flowing air. In terms of droplet breakup, the co-flowing air doesn’t actually seem to have a major effect on the electrospray. This could be due to the low co-flowing air velocity combined with the relatively small droplets (<100um) that are formed by an electrospray overall, regardless of the operating mode. If this is the case, then the benefits of using the co-flowing gas in mass spectrometer applications must be to direct and guide the spray into the mass spectrometer inlet, rather than significantly enhance the spray breakup. However, in the cases where a relatively large electrospray nozzle is used, and also where the liquid flow rates are even higher than those tested here, it would be expected that the co-flowing air would have more of an effect on spray breakup.

Figure 7-12: Spray flux measurements at the location of maximum detected flux for each spray mode.
Figure 7-12 shows the measured spray flux average for each case. This is the flux calculated by the PDPA system directly. One point to note is that in order for the PDPA system to calculate flux values, it has to first determine the volume of the measurement that is created by the interference of its laser beams. This calculated volume has to be verified through intensive iteration on the system to validate the measurements. In our experiment, however, the spray flux value was used in a more relative sense, to determine which modes and conditions produced higher fluxes, and the actual accuracy of the numerical value was irrelevant. It can be seen in 7-11, that in the spindle and cone-jet mode, the spray flux is minimally effected by the co-flowing air. In contrast, there is a significant effect in the unstable modes. With the use of co-flowing air, in the spindle and cone-jet modes, the droplet are directed in a more focused direction, however, the droplet density is similar. In the unstable mode, without co-flowing air, the produced doplets have an extremely low density, however, with the addition of co-flowing air, the produced droplets are all directed in a similar direction, greatly increasing the droplet density and hence the spray flux.

In order to look at the details of the spray distribution for each mode, the histogram data for diameter and velocity is shown in the following figures. For the spindle and cone-jet modes, the data is from the entire planar scan, and for the unstable modes, it is from the linear scan.
Figure 7-13: Spindle mode PDPA data. Experiment conditions: 7 microliter/min flow rate of 75% aqueous methanol.
For the spindle mode of electrospray operation, a bimodal droplet diameter distribution can be seen in both the nebulized and un-nebulized case. This means that there are two distinct droplet diameter averages within the same spray cross-section. In Figure 7-13-1A, the bimodal distribution shows averages of around 10 microns and 20 microns. There are a higher percentage of smaller 10 micron droplets, as expected from the previous discussion. In Image 1B, the distribution is still bimodal. However, the percentage of small and large droplets is different. In this case, there seems to be a higher percentage of larger droplets with a mean of around 20 microns. This bimodality is explained by looking at the jet breakup mechanisms for the spindle mode. This mechanism typically produces many smaller droplets, as well as a few large droplets, simultaneously below the emitter. Without co-flowing air, the diameter histogram has a larger percentage of smaller droplets. With the addition of co-flowing air, there is a shift towards the larger diameter droplets produced. Another effect of the co-flowing air can be seen in the axial velocities of the droplets. Without co-flowing air, there is a narrower distribution of fast moving drops. With the addition of co-flowing air, this distribution is broadened in addition to the average velocity in the axial direction being increased. In Figure 7-13-3A and 4B, the droplet diameter vs. droplet axial velocities is shown. These charts show that with the introduction of co-flowing air, all the droplets increase in velocity. In Figure 7-13-3B, the minimum speed that all the droplets are traveling is approximately 8 m/s with one or two exceptions. In contrast, without co-flowing air, there are many droplets travelling slower than 5 m/s and even some that are in the 1-2 m/s range. Figure 7-13-4A and B shows the radial velocity component of the droplets. Without co-flowing air in Figure 7-13-4A, it can be seen that the average radial component is almost 0 m/s, and that the individual maximum speeds seem to be around 7 m/s and -7 m/s. The radial speeds are balanced in both directions, indicating a fairly symmetric spray pattern. Figure 7-13-4B shows the co-flowing air shifting the radial velocity distribution to an average of -2 m/s. This indicates the spray moving away from the central axis under the influence of the co-flowing air. Also, the distribution of the velocities in the radial direction is much narrower with the effect of co-flowing air. Figure 7-13-5A and B verify the previous observation. The co-flowing air clearly shifts the distribution downwards and also narrows it.
Figure 7-14: Cone Jet mode PDPA data. Experiment conditions: 7 microliter/min flow rate of 75% aqueous methanol.
In the cone-jet mode of electrospray operation, the co-flowing air broadens the droplet distribution slightly. The majority of the droplets produced are still extremely small and uniform. However, the co-flowing air seems to create a few droplets in the 1 to 15 micron range. This is shown in Figure 7-14-3B and 5B, and cannot be easily explained if you observe the optical images of the cone-jet mode. However, although the cone jet appeared to be stable in the optical images, even with the addition of nebulized air, it is very likely that larger drops may have been emitted intermittently. The velocity distribution is broadened because some drops move faster with the addition of co-flowing air, while some move slower. This can be related to the aerodynamic effect on the droplets compared to droplet size, as discussed in section 3.3, where it is discussed that the larger the droplets, the larger the aerodynamic effect. Using this explanation, the larger sized droplets in the cone-jet distribution should be accelerated by the co-flowing air, and the smaller moving drops should remain un-affected. However, this is not the case, as the smaller droplets seem to have slowed down even further.
Figure 7-15: Unstable mode PDPA data. Experiment conditions: 7 microliter/min flow rate of 75% aqueous methanol.
At extremely high electric field strengths, the unstable mode of electrospray operation is observed. As the name suggests, there is no real pattern to the way the electrospray operates in this mode. In fact, there is very little literature on this mode in general. This makes the unstable mode very difficult to study. Any Nanolite flash images taken in this mode show either a ligament ejected in a random direction directly from the meniscus or liquid in the meniscus with unstable surface waves, most likely due to the intense electric field forces. Figure 7-15 shows the measured diameter and axial velocity histograms for the unstable mode of electrospray operation. At the lower flow rate, the droplet distribution shows various peaks around the 15, 30 and 45 um diameter regions. In the high flow rate mode, there are also multiple peaks; however, there is a slight shift towards the smaller diameters. To explain this shift, we can refer back to the discussion on the aerodynamic effects on liquid drops in section 3.3. The critical surface tension $\sigma_{cr}$ is related to the droplet diameter. The larger the droplet diameter, the larger the critical surface tension and, therefore, the larger the aerodynamic effect on the droplet. Also shown in Figure 7-15 is the radial velocities. In the unstable mode, without co-flowing air, the radial velocities are centered on 0 m/s. With the addition of co-flowing air, there is a slight increase in the radial velocity mean, which indicated the spray structures being influence by the co-flowing air.
Figure 7-16: Unstable mode PDPA data. Experiment conditions: 500 microliter/min flow rate of 75% aqueous methanol.
The final data set in Figure 7-16 shows the high liquid flow rate unstable mode of electrospray operation. One immediate observation is that compared to the low flow rate unstable mode, shown in Figure 7-15, the number of measured values is significantly higher. This can be attributed to the much higher liquid flow rate. Without the addition of co-flowing air, the distributions of all the characteristics, is very similar to the low flow rate unstable air; however with significantly more measured values. With the addition of co-flowing air the distributions are modified in the same manner as the low flow rate mode.

7.6 Aerodynamic Effects

In Figure 7-17, the calculated Weber numbers for all of the various electrospray modes are presented. Two parameters that influence the Weber number are the droplet size and droplet velocity. In order for the Weber number to increase, the droplet diameters must increase, while the droplet axial velocity should reduce. The case of an unstable, low flow rate electrospray meets both these conditions, resulting in the largest Weber number. The second largest Weber number is in the high flow rate unstable mode. In this case, the hydrostatic pressure from the fluid helps drive it out from the emitter at a higher initial velocity.
8 Conclusions

The specific operating modes for an electrospray used in a mass spectrometer have been identified and recorded using optical imaging. Two types of methanol aqueous solutions were used, 50% and 75% respectively. A range of flow rates from 1 to 1200 µl min\(^{-1}\) and a range of voltages from 0 to 5000 V were run. From the results presented, it can be seen that a range of operating modes exist for this particular electrospray system, and also that these modes are highly dynamic. With the naked eye, it is very difficult to determine or distinguish these modes because these phenomenon occur so rapidly and because the spray itself is very small. However, through the use of a high speed camera, Digital SLR Camera, Nanolite flash and a long distance microscope these modes could be recognized. For a 50% methanol aqueous solution, no stable cone-jet mode could be achieved, while for the 75% solution, the cone-jet mode was achieved for every flow rate up to 16 µl min\(^{-1}\). Beyond this limiting flow rate, only unstable modes such as the ramified jet and kink instabilities existed. There are many factors that could explain why no cone-jet is achieved with the 50% solution and it is reasonable to assume that the difference in fluid properties is a major one, as this has already been identified by other researchers through experiments using a variety of fluids [11] [10]. The next set of experiments introduce co-flowing air as a parameter and study its affect on the electrospray. Finally, once we have the operating modes characterized for both an un-nebulized and nebulized electrospray, a PDPA system was used to determine droplet size, droplet velocities, number concentrations and also turbulence intensities for a nebulized and un-nebulized electrospray. In general, the effect of co-flowing air on droplet diameter is dependent on the droplet size. For larger droplets, the co-flowing air tends to decrease the average droplet diameter while for a smaller droplet the diameter is increased slightly. This increase in droplet size for the smaller initial droplets can be attributed to the droplet arrival time at the PDPA measurement location and also the evaporation rate, with the addition of co-flowing air. One major effect of the co-flowing air is the significant affect on the concentration of droplets in the spray core. For small diameter spindle and cone-jet mode sprays, the concentration is reduced dramatically, while for a larger diameter unstable mode spray, the concentration is increased. Another effect of the co-flowing air is the fact that it makes the droplet size much more uniform in the high flow rate unstable mode. This can be attributed to the fact that the larger droplets in the unstable more are more susceptible to shearing type breakup due to the air turbulences and the general air flow.
9 Future Work

The field of electrosprays is enormous. One study cannot even begin to understand the phenomenon present. To fully appreciate the characteristics of such sprays, the integration of numerous works must be done. By carrying out the work described in this paper, many aspects for further research have been realized. Some of these aspects have already been the subject of intensive work in the past, while others have only just been touched upon. The following list summarizes the future work that has been identified through the project:

1) Numerical

   a) The effect of charge on the electrospray jets has to numerically be studied further. In particular, there should be more studies done on the electric field interaction with various parts of the jets produced.

2) Varying flowrates

   a) In this study, the flowrates for the liquid and co-flowing air were studied so that all modes of electrospray could be observed. Further investigations into the higher liquid flow rate, high voltage electrosprays should be studied in a similar manner. One major issue with the higher air flowrates was identified in this work. This is that the spray cannot be visualized due to the extremely high air velocities. However, using a PDPA system, spray statistics can be measured

3) Image Analysis

   a) The image analysis techniques used can be further refined to improve the quality of results and also to be able to process more data.
Bibliography


## Nomenclature

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<th>Symbol</th>
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<td><strong>ES</strong></td>
<td>electrospray</td>
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<td>diameter of drop</td>
<td>[m]</td>
</tr>
<tr>
<td><strong>D_j</strong></td>
<td>diameter of jet</td>
<td>[m]</td>
</tr>
<tr>
<td><strong>q</strong></td>
<td>charge of a drop</td>
<td>[C]</td>
</tr>
<tr>
<td><strong>q_v</strong></td>
<td>Vonnegut charge</td>
<td>[C]</td>
</tr>
<tr>
<td><strong>q_r</strong></td>
<td>Rayleigh charge</td>
<td>[C]</td>
</tr>
<tr>
<td><strong>v</strong></td>
<td>volume of a drop</td>
<td>[m³]</td>
</tr>
<tr>
<td><strong>I</strong></td>
<td>current in the electrospray circuit</td>
<td>[C s⁻¹]</td>
</tr>
<tr>
<td>Symbol</td>
<td>Description</td>
<td>Unit</td>
</tr>
<tr>
<td>--------</td>
<td>-------------</td>
<td>------</td>
</tr>
<tr>
<td>R</td>
<td>drop radius</td>
<td>[m]</td>
</tr>
<tr>
<td>R_g</td>
<td>gas constant</td>
<td>[JK^{-1}mol^{-1}]</td>
</tr>
<tr>
<td>N</td>
<td>number of elementary charges</td>
<td></td>
</tr>
<tr>
<td>K</td>
<td>experimentally determined parameter for droplet evaporation</td>
<td></td>
</tr>
<tr>
<td>k</td>
<td>experimentally determined parameter for Rayleigh jet breakup</td>
<td></td>
</tr>
<tr>
<td>k_i</td>
<td>ion emission rate</td>
<td></td>
</tr>
<tr>
<td>U_r</td>
<td>relative velocity</td>
<td>[ms^{-1}]</td>
</tr>
<tr>
<td>U_v</td>
<td>thermal velocity of solvent vapor</td>
<td></td>
</tr>
<tr>
<td>P_e</td>
<td>electric pressure</td>
<td>[Nm^{-2}]</td>
</tr>
<tr>
<td>W_e</td>
<td>Weber’s Number</td>
<td></td>
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<tr>
<td>W_ecr</td>
<td>critical Weber’s Number</td>
<td></td>
</tr>
<tr>
<td>P</td>
<td>pressure</td>
<td>[Nm^{-1}]</td>
</tr>
<tr>
<td>λ</td>
<td>wavelength</td>
<td>[m]</td>
</tr>
<tr>
<td>a</td>
<td>unperturbed jet radius</td>
<td>[m]</td>
</tr>
<tr>
<td>r_s</td>
<td>perturbed jet radius</td>
<td>[m]</td>
</tr>
<tr>
<td>α</td>
<td>perturbation amplitude</td>
<td>[m]</td>
</tr>
<tr>
<td>ω_0</td>
<td>uniform jet velocity</td>
<td>[ms^{-1}]</td>
</tr>
<tr>
<td>u_i</td>
<td>velocity in the i^{th} direction</td>
<td></td>
</tr>
<tr>
<td>q</td>
<td>u_iu_i</td>
<td></td>
</tr>
<tr>
<td>F_{EP}</td>
<td>electric pressure</td>
<td>[Nm^{-1}]</td>
</tr>
</tbody>
</table>
Appendix

11 Fluid Properties

The following table gives the properties of the various fluids used in our experiments [47][13]:

<table>
<thead>
<tr>
<th>Liquid</th>
<th>$\rho$ (kg/m$^3$)</th>
<th>$\mu$ (kg/(m-s))</th>
<th>$\gamma$ (N/m)</th>
<th>$\sigma$ (S/m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>998</td>
<td>1x10$^{-3}$</td>
<td>7.28x10$^{-2}$</td>
<td>4x10$^{-4}$</td>
</tr>
<tr>
<td>50% Aqueous Methanol</td>
<td>916</td>
<td>-</td>
<td>3.33x10$^{-2}$</td>
<td>-</td>
</tr>
<tr>
<td>75% Aqueous Methanol</td>
<td>859</td>
<td>-</td>
<td>2.65x10$^{-2}$</td>
<td>-</td>
</tr>
<tr>
<td>Methanol</td>
<td>791</td>
<td>5.94x10$^{-4}$</td>
<td>2.25x10$^{-2}$</td>
<td>4.4x10$^{-5}$</td>
</tr>
</tbody>
</table>

Table 11-1: Table showing the fluid properties of Water and Methanol

12 Electric Field at Capillary

The following figure shows the relationship between applied voltage and electric field intensity at the emitter based on equation (1-7).

![Electric Field at Capillary](image)

Figure 12-1: Relationship between voltage applied to emitter and electric field intensity.
13 Experiment Conditions

13.1 Optical Observation and PDPA Measurements

The following tables list the detailed experimental conditions for the optical observation with the Nanolite flash equipment setup and the PDPA measurements as well as a PDPA summary of results.

<table>
<thead>
<tr>
<th>Case No.</th>
<th>Liquid Flow rate (μl/min)</th>
<th>Methanol % in Aqueous Solution</th>
<th>Air Flow rate Std ml/min</th>
<th>Air Pressure (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O 1-1</td>
<td>6</td>
<td>75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O 1-2</td>
<td>10</td>
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</tr>
<tr>
<td>O 1-3</td>
<td>4</td>
<td>75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O 1-4</td>
<td>2</td>
<td>75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O 1-5</td>
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<td>75</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>O 2-1</td>
<td>5</td>
<td>75</td>
<td>100</td>
<td>4.5</td>
</tr>
<tr>
<td>O 2-2</td>
<td>2</td>
<td>75</td>
<td>100</td>
<td>4.5</td>
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<tr>
<td>O 2-3</td>
<td>4</td>
<td>75</td>
<td>100</td>
<td>4.5</td>
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<td>4.5</td>
</tr>
<tr>
<td>O 3-1</td>
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<td>75</td>
<td>200</td>
<td>11</td>
</tr>
<tr>
<td>O 3-2</td>
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<td>75</td>
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<td>11</td>
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<tr>
<td>O 3-3</td>
<td>4</td>
<td>75</td>
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</tr>
<tr>
<td>O 3-4</td>
<td>2</td>
<td>75</td>
<td>200</td>
<td>11</td>
</tr>
<tr>
<td>O 3-5</td>
<td>1</td>
<td>75</td>
<td>200</td>
<td>11</td>
</tr>
<tr>
<td>O 4-1</td>
<td>6</td>
<td>75</td>
<td>300</td>
<td>19.5</td>
</tr>
<tr>
<td>O 4-2</td>
<td>2</td>
<td>75</td>
<td>300</td>
<td>19.5</td>
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<td>75</td>
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<td>19.5</td>
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<td>O 4-5</td>
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<td>75</td>
<td>300</td>
<td>19.5</td>
</tr>
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</table>

Table 13-1: Experimental Conditions for Optical Analysis.
<table>
<thead>
<tr>
<th>Case No.</th>
<th>Liquid Flow rate (µl/min)</th>
<th>Methanol % in Aqueous Solution</th>
<th>Air Flow rate Std ml/min</th>
<th>Air Pressure (PSI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-1</td>
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<td>0</td>
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<td>75</td>
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<td>0</td>
</tr>
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<td>75</td>
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<td>0</td>
</tr>
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<td>75</td>
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<td>0</td>
</tr>
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<td>0</td>
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<td>75</td>
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<td>4.5</td>
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</tr>
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<td>0</td>
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<tr>
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<td>4-8</td>
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<td>75</td>
<td>200</td>
<td>11</td>
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</table>

Table 13-2: Experimental Conditions for PDPA Analysis
<table>
<thead>
<tr>
<th>Case Number</th>
<th>Electrospray Mode</th>
<th>Voltage (V)</th>
<th>Liquid Flow rate (μl/min)</th>
<th>Air Flow rate (Std ml/min)</th>
<th>D10 (μm)</th>
<th>D32 (μm)</th>
<th>Axial Velocity (m/s)</th>
<th>Radial Velocity (m/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P 4-1</td>
<td>Spindle</td>
<td>2600</td>
<td>7</td>
<td>0</td>
<td>13.38</td>
<td>18.43</td>
<td>10.36</td>
<td>-0.24</td>
</tr>
<tr>
<td>P 4-2</td>
<td>Cone Jet</td>
<td>3400</td>
<td>7</td>
<td>0</td>
<td>2.53</td>
<td>2.95</td>
<td>14.32</td>
<td>1.31</td>
</tr>
<tr>
<td>P 4-3</td>
<td>Unstable</td>
<td>4400</td>
<td>7</td>
<td>0</td>
<td>29.17</td>
<td>36.10</td>
<td>4.82</td>
<td>-0.02</td>
</tr>
<tr>
<td>P 4-4</td>
<td>Spindle</td>
<td>2600</td>
<td>7</td>
<td>200</td>
<td>18.19</td>
<td>23.42</td>
<td>20.58</td>
<td>-2.38</td>
</tr>
<tr>
<td>P 4-5</td>
<td>Cone Jet</td>
<td>3400</td>
<td>7</td>
<td>200</td>
<td>3.36</td>
<td>16.78</td>
<td>14.46</td>
<td>0.69</td>
</tr>
<tr>
<td>P 4-6</td>
<td>Unstable</td>
<td>4400</td>
<td>7</td>
<td>200</td>
<td>26.84</td>
<td>36.50</td>
<td>14.99</td>
<td>0.02</td>
</tr>
<tr>
<td>P 4-7</td>
<td>High Flow Rate Unstable</td>
<td>5000</td>
<td>500</td>
<td>0</td>
<td>24.18</td>
<td>34.69</td>
<td>8.35</td>
<td>0.16</td>
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<tr>
<td>P 4-8</td>
<td>High Flow Rate Unstable</td>
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<td>500</td>
<td>200</td>
<td>24.21</td>
<td>35.60</td>
<td>13.79</td>
<td>0.00</td>
</tr>
</tbody>
</table>

Table 13-3: Summary of PDPA measurements
14 PDPA Data

14.1 Surface Plots

The following images show surface plots of all the measured PDPA data. This format representing the data can be helpful to visualize the spray structures.

14.1.1 Diameters Isometric View
14.1.2 Diameters X-Y View

14.1.3 Diameters X-Z View
14.1.4 Diameters Y-Z View

14.1.5 Velocity in Z Isometric View
14.1.6 Velocity in Z X-Y View

![Graphs showing velocity in Z X-Y View: Case 4.1 - Pulsating - No Air - Velocity in Z and Case 4.4 - Pulsating - Air - Velocity in Z.](image)

14.1.7 Velocity in Z X-Z View

![Graphs showing velocity in Z X-Z View: Case 4.1 - Pulsating - No Air - Velocity in Z and Case 4.4 - Pulsating - Air - Velocity in Z.](image)
14.1.8 Velocity in Z Y-Z View

14.1.9 Velocity in Y Isometric View
14.1.10 Velocity in Y X-Y View

14.1.11 Velocity in Y X-Z View
14.1.12 Velocity in Y Y-Z View

14.1.13 Number Concentration Isometric View
14.1.14 Number Concentration X-Y View

14.1.15 Number Concentration X-Z View
14.1.16 Number Concentration Y-Z View

14.1.17 Turbulence Intensities in Z Isometric View
14.1.18 Turbulence Intensities in Z X-Z View

14.1.19 Turbulence Intensities in Z X-Z View
14.1.20 Turbulence Intensities in Z Y-Z View

14.1.21 Turbulence Intensities in Y Isometric View
14.1.22 Turbulence Intensities in Y X-Y View

14.1.23 Turbulence Intensities in Y X-Z View
14.1.24 Turbulence Intensities in Y Y-Z View